A NEW SCHOOL CHEMISTRY

W. LITTLER

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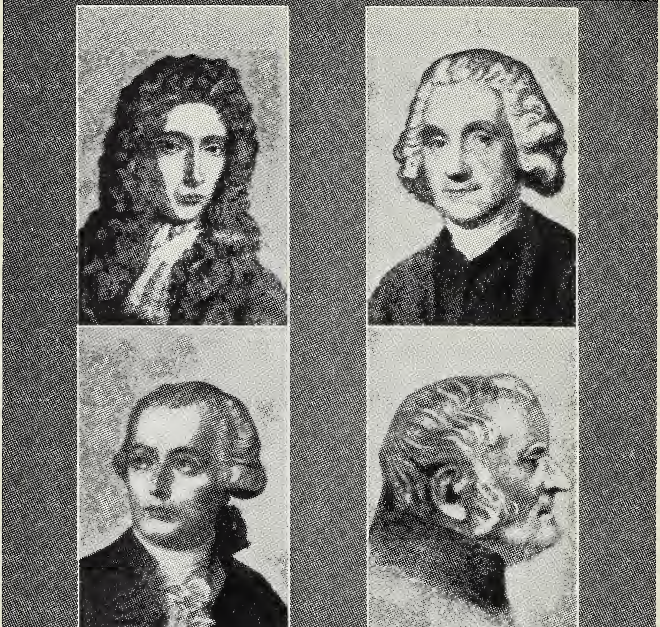
A NEW
SCHOOL CHEMISTRY



SOME FAMOUS CHEMISTS (*see footnote, p.* 530)

Robert Boyle Joseph Priestley
Antoine Lavoisier John Dalton
Amadeo Avogadro Dmitri Mendeléeff Marie Curie

A NEW
SCHOOL CHEMISTRY

By

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TO
MY WIFE

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PREFACE

It is now some twenty-five years since I wrote *Elementary Chemistry*. During that period I have revised it from time to time, but have always had in mind the desirability of keeping the page-numbering unaltered, at least for the greater part of the book. Otherwise, a teacher ordering replacement copies would find himself in a difficult and irritating situation.

The condition just mentioned is, however, a hampering one, and it was impossible to make a number of changes and additions that were in themselves desirable. It seemed in fact that the time had arrived for a much more considerable revision. Nevertheless, it was felt that a number of schools might well wish to continue with the older book, at least for some time, and that it would be better to keep *Elementary Chemistry* in print, producing the revised edition as a new book with a distinguishing title. That is the origin of *A New School Chemistry*.

Anyone familiar with the earlier volume will recognise that some chapters have been left unaltered, while others have been completely re-written. Between these extremes there have been changes of very varying degrees of magnitude.

Many teachers have to consider the extent to which a given text-book meets the requirements of examinations such as matriculation or G.C.E. (Ordinary Level). I believe that in this respect both *Elementary Chemistry* and *A New School Chemistry* will be found to be fully adequate. I have had in mind, however, that keen students are never content to keep strictly to the beaten track, but like a chance, at least now and then, to survey neighbouring territory or to contemplate distant horizons. The Introduction, the chapter on Organic Chemistry and much of that on 'The Atom since Dalton' will illustrate what I mean, and in the present volume this more liberal outlook receives fuller expression.

In a book dealing with chemistry, considerable attention must always be paid to certain manufacturing processes. These alter from time to time, and in this new book I have tried to embody the most recent developments.

Besides the changes already indicated, I may add that most of the photographs and a number of the line diagrams are new, as are the majority of the questions, chiefly taken from recent G.C.E. papers. For permission to use these, I wish to thank all the eight examining bodies concerned, and in addition The Controller of H.M. Stationery Office for permission to use questions set at examinations for the Scottish Leaving Certificate.

I have received much help from various manufacturing companies, associations of manufacturers etc., and would like to record my debt to Acheson Colloids Ltd., Albright and Wilson Ltd., The Aluminium Development Association, The Associated Ethyl Co. Ltd., The Atomic Research Establishment, The British Iron and Steel Federation, The Copper and Brass Research Association (New York), The Copper Development Association, Imperial Chemical Industries Ltd., The Lead Development Association, Midland Silicones Ltd., The National Coal Board, The National Sulphuric Association Ltd., The Nitrate Corporation of Chile Ltd., The Tennessee Valley Authority, The Water Companies' Association and the Zinc Development Association. I would like to add that on the frequent occasions when I have sought their aid, I have found the staff of the Bristol Reference Library most courteous and helpful.

In a number of cases I have submitted my typescript to an expert connected with one or other of the above firms or associations, and have greatly benefited from the criticisms and suggestions received. Further, I would like to express my indebtedness to that storehouse of the collected wisdom of hundreds of fellow-teachers, *The School Science Review*. I have had much help too from individuals with whom I have corresponded or whom I have interviewed. They are too numerous for separate record here, so I will ask them please to accept this general reference in addition to the personal letter of thanks they have already received.

Bristol, W. L.
January 1957

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INTRODUCTION

CHEMISTRY IN OUR DAILY LIFE

Chemistry had its beginnings, probably in Egypt, in the needs of daily life. In that country, for religious reasons, men set a high value on the discovery of substances which would preserve a body from decay and, no doubt after many failures, they achieved some striking successes. They were interested, too, in dyes and in medicines, and doubtless made many trials with plant juices, etc., in their attempts to secure what they wanted. Sometimes a lucky discovery was made by accident, as when a fire happened to be kindled in close contact with soda and a suitable sand, yielding glass; or in contact with the ore *galena*, when lead might easily be produced.

Thus men came to have a keen interest not only in the materials around them, but also in new substances which could be obtained by heating these materials with fire or treating them in other ways. We have in fact the beginnings of a kind of practical chemistry.

And now we come to a remarkable fact. If we imagine ourselves 'taking stock' about the year 1600, i.e. 5000 years or so after the early Egyptian days of which we have been speaking, we are struck with the comparatively small number of 'chemical' discoveries that were made in all those fifty centuries; small at least in comparison with what we find at the present time—less than four centuries later—when discoveries have become so numerous that it would be a very formidable task indeed to make a complete list of them. Why should progress have been so much greater in the last three or four centuries than in all the preceding fifty?

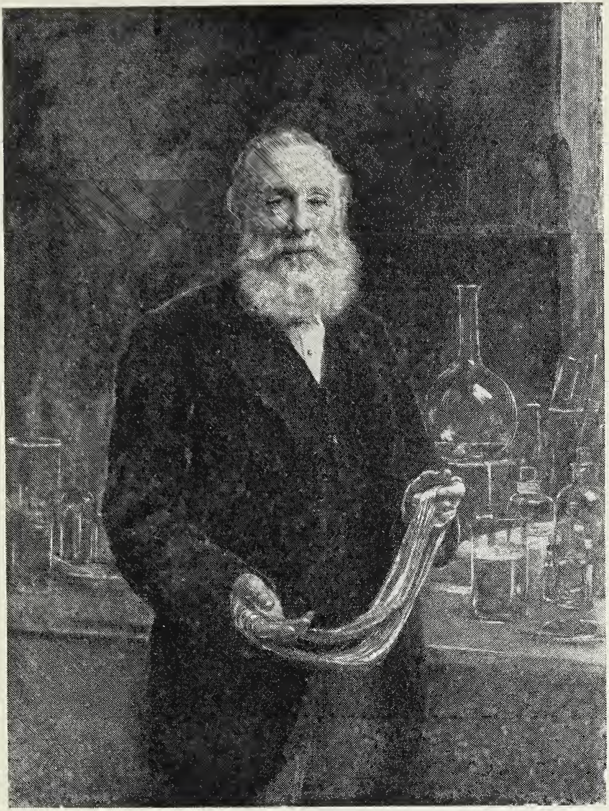
The answer is that roughly in the neighbourhood of the year 1600, for reasons which we cannot discuss just now, men began to study chemistry from a different motive. Hitherto, they had worked chiefly to secure some material gain—to make gold out of lead perhaps, or to prepare some wonderful medicine. Now they began to study it for its own sake.

They tried to *understand* instead of trying to *obtain*. Robert Boyle, for instance, in his *Sceptical Chymist* (1661), maintained that chemistry was worth studying with no other object than to find out the true composition of substances.

As a result of this new attitude, men gradually arrived at *theories* which would stand the test of experiment—Lavoisier's theory of combustion, for instance, about 1780, and Dalton's Atomic Theory (1807). A sound theory is like a good foundation. It is something on which one can build, and building has been very rapid. New discoveries, often of great practical use, are being made at an almost bewildering rate. The strange but understandable thing is that so long as men studied chemistry simply for material gain, that gain was small. When they abandoned that motive and studied it for its own sake, they acquired not only knowledge but great material gain in addition.

One hopes that the boys and girls who read this book will, like good chemists, find the subject worth studying for its own sake. At the same time it is refreshing and encouraging to pause sometimes and consider how man in his daily life is being helped by the discoveries of the chemist, and this we shall do in the next few pages. Among the thousands of examples it is difficult to make a selection. Our illustration (p. 3) is connected with the manufacture of dyes, but except for this we will confine ourselves to a few discoveries which have a wide application to the questions of food supply, clothing and the preservation or restoration of health. Let us begin with one or two matters related to food supply.

In 1898 Sir William Crookes, one of the world's greatest scientists, aroused widespread alarm by an address which he made to the British Association. In this address he drew attention to the fact that the world's demands for wheat were continually increasing, and that the soil was able to produce this wheat only if it were regularly supplied with 'fixed nitrogen,' i.e. *not* the nitrogen of the air, which is in the free condition, but nitrogen in combination with other elements. The only really large supply of fixed nitrogen consisted of 'Chile saltpetre'—sodium nitrate, $NaNO_3$. Sir William estimated that at no very distant date supplies of this would



Sir William Perkin

From a painting by A. S. Cope in the National Portrait Gallery London

W. H. Perkin was only 18 when, working in a laboratory which he had fitted up at home, he prepared the first coal-tar dyestuff (mauve). Encouraged by his success, he attacked all the difficulties connected with business and manufacture, and laid the foundations not only of the great synthetic-dye industry, but of the organic-chemistry industry in general. The illustration represents him as holding up some material coloured with his new dye.

begin to run short, and after that time the earth would be unable to feed its population; we should be faced with world famine. He suggested that chemists should try to find some way of making the nitrogen of the air combine with other elements, so turning it into the necessary fertilizer.

His advice was taken, and several very successful processes have been worked out. In the one chiefly in use, atmospheric nitrogen is made to combine with hydrogen, forming the gas ammonia, NH_3. From this it is a very easy matter to prepare ammonium sulphate, a substance which, by the bacteria present in the soil, is readily turned into the necessary nitrates.

By the production of fertilizer the chemist is, of course, assisting in the growth of food. It is natural to ask whether he will ever be able to manufacture it directly. After all, foods consist of compounds of a very few elements (chiefly carbon, hydrogen, oxygen and nitrogen). Would it not be possible to make these compounds in the factory?

Some progress has been made, especially in the manufacture of fats. It should be mentioned that many of the oils obtained from fish, on an enormous scale, are quite unsuitable for human food, or even for the manufacture of soap. About the year 1900, the French chemist Sabatier showed that by suitable treatment with hydrogen, using nickel as a catalyst, these oils could be turned into hard fats suitable for making soap, and in many cases for the manufacture of margarine.

Although the process just mentioned is of great practical use because it enables us to turn an inedible product into a food, it can fairly be objected that the manufacture is only partial. We start not from the elements carbon, hydrogen, etc., but from compounds already present in the fish. Now, however, a process has been partly worked out in which we really start from the elements.

By the action of hydrogen under certain conditions, the carbon present in coal is turned into hydrocarbons, and these can be oxidised to what are known as fatty acids. The latter are easily made to react with glycerine, forming a mixture of fats (the glycerine, $C_3H_5(OH)_3$, could if necessary be made from its elements).

The mixture is a sort of margarine, but not very good, for it is found that the human body can digest only about 50 per cent. of it. The fact is that of the fatty acids mentioned above, some contain an even number of carbon atoms in the molecule, and some an odd number—and the body can digest only the 'evens'. However, we have evidently gone a long way towards the production of a true synthetic food, and in time the problem will no doubt be completely solved.

To this problem of the manufacture of food there is another line of approach which is being persistently followed. In the plant, sugar and starch are made from very simple materials—carbon dioxide (obtained from the air) and water. Sunlight as a source of energy is certainly essential, and it is believed that in the chain of reactions, phosphorus compounds derived from the soil play a necessary part. Here is a clear challenge to the chemist, and he is working hard to carry out in the laboratory a process that goes on so easily in nature. The manufacture of sugar seems to be the key problem. If he can succeed here, he can see his way to the preparation of many other foods at present obtained only from the vegetable kingdom. He *can* make sugar, but only by very cumbrous and costly methods. He still has to discover the secret of the plant, but he is full of hope.

From the question of food let us now turn to that of clothing. Until comparatively recently man clothed himself entirely with products derived from the animal or vegetable kingdom—furs, wool, silk, cotton, linen, etc. In 1898 two chemists, Cross and Bevan, patented a process in which the cellulose of which wood largely consists is converted into a silk-like fibre known as rayon or viscose. The cellulose is first heated with a mixture of caustic soda solution and carbon disulphide. A viscous liquid is obtained, which is then squirted through very fine jets into a regenerating solution containing sulphuric acid and certain other substances—'regenerating,' because the effect is to reproduce the original cellulose, but in the form of fine, silky filaments which are easily spun into threads or yarn suitable for weaving. In a big rayon factory one can see an incoming stream of lorries loaded with wood-pulp, which has been made from the trees of Norway or Canada, while from another gate a few hundred yards away are streaming out more lorries carrying away artificial silk of every colour.

Rayon is an example of a 'partly synthetic' fibre, because the chemist has used as his starting point a natural substance of complicated structure (cf. the production of edible fat by Sabatier's process). But 'wholly synthetic' fibres are now being made. A familiar example is nylon, in which the chemist uses certain hydrocarbons as his basic material. We use the term 'wholly synthetic' because he could if required make these hydrocarbons from their elements, though in practice he extracts them from coal tar or petroleum because he finds it cheaper to do so. Another well-known example of a wholly synthetic fibre is terylene.

It seems unlikely that synthetic fibres will ever completely displace natural ones. There is a place for both. The final result may be that man will continue to use natural textiles for his more basic needs, while for artistic effect, or where some particular property is required, he will employ one or other of the synthetic fibres.

Let us now consider the part played by the chemist in maintaining or restoring health. At the outset we may notice that here we are very often concerned with team work, in which the chemist is associated with the physician, surgeon, bacteriologist, etc.

We will begin with the familiar substance chloroform ($CHCl_3$), discovered by the chemist Liebig in 1831, but first used as an anæsthetic by Sir James Simpson in 1847.

Before 1847 serious operations were comparatively rare because of the unbearable pain. Now that they could be carried out painlessly they became much more common—and then another very serious trouble arose. In hundreds of cases the wound of the operation became what we should now call 'septic'—poisoned in some way that the doctors could not then understand—and the patient died of what was often called 'hospital gangrene.'

A great surgeon named Joseph Lister believed that the gangrene was caused by a certain germ getting into the wound and multiplying at a great rate. If he could kill the germ, he ought to be able to save the patient's life. Once again it was a product of chemistry which saved the situation, for Lister discovered that germs could not live in carbolic acid or phenol, C_6H_5OH. By the proper use of a solution of phenol the wound was kept free from germs and soon healed up. There is no need to make exaggerated claims. Lister's discovery was, first and foremost, a triumph of surgery, but it was chemistry which provided him with an essential weapon. If we say that his discovery has saved thousands of lives, we are certainly well within the mark, and probably we should not be going beyond it if we said millions.

We may add that nowadays antiseptic treatment has given place almost entirely to *a*septic treatment, i.e. the surgeon aims not so much at killing harmful germs, but at working under conditions of such extreme cleanliness that they never enter the wound in the first instance.

It was not long before scientists recognised that many diseases besides 'hospital gangrene' were due to the action of micro-organisms which we will continue to call simply 'germs.' This is a rather rough-and-ready term, for actually a number of very different classes are concerned; bacteria and viruses for instance; but it will serve our present purpose.

They may enter the body in various ways. Sometimes we breathe them in (e.g. tuberculosis), sometimes they are introduced into the body by the bite of an insect, as in malaria through the bite of a mosquito, and so on. Very seldom (in England) water is infected with the germs of typhoid. It is easily sterilised, say, by the use of chlorine, which kills the germs. Armies have often suffered great losses from disease due to contaminated water. In the Crimean War, 1854–56, many of our soldiers died from cholera, and as late as 1899–1902, in the Boer War, there were actually more of our men killed by typhoid than by the action of the enemy.

If harmful germs can be killed, why not dispose of them by dosing the infected person with something that will kill them? The answer is, of course, that you might easily kill the patient as well as the germs. Still, the direction of possible advance is clear. The chemist has to search for a substance that while deadly to the invading germ is not seriously harmful in other ways. Actually the difficulties are immense, but some great successes have been achieved. During the Second World War, for instance, a very serious situation arose when Java fell into the hands of the Japanese, and supplies of quinine began to run short (quinine is obtained from the cinchona plant, grown chiefly in Java—and quinine was the standard remedy for malaria). Before long the chemist had produced several very effective synthetic remedies, such as atebrin, issued to our troops in Burma and the Far East. A little later (1945) paludrin was prepared, and appears to be more effective than any other drug in the treatment of malaria. We may mention here that such discoveries are not simply of war-time importance. Although in our own country we seldom hear of a case of malaria, it has been estimated that in the world as a whole nearly half the deaths are due directly or indirectly to this disease.

Then there is the case of *penicillin.* Sir Alexander Fleming, a medical bacteriologist, noticed that the trays of gelatine, etc., in which he was cultivating various strains of bacteria often showed patches where the bacteria had been destroyed. What had killed them? Investigation showed that a hostile germ was at work, produced by a mould, *penicillium notatum*, which had accidentally drifted into his cultures (probably from a nearby stable!). It was suspected that the bacteria-killing effect was caused by some definite compound produced by *p. notatum*, and the problem was if possible to isolate this compound. Here was a job for the chemists, and after several years' work they succeeded in isolating the now familiar penicillin. This is found to be very effective in killing a number of varieties of germs which may have invaded the human body, without injury to the body itself.

Not all illnesses are caused by the invasion of germs. Doctors recognise a large number of 'deficiency diseases'—diseases due to the absence of some particular compound. One of the most familiar examples is scurvy. It has been known for centuries that this disease is connected with the absence of some substance present in fresh vegetables and in fruit juices (especially orange, lemon, etc.), but it was not till 1912 that the problem began to be completely unravelled. It was found that in the absence of a compound now known as *vitamin C* (which occurs in the fruit juices), scurvy may develop. The pure substance was isolated in 1932.

Another deficiency disease is beri-beri, caused by the absence of vitamin B_1. The story is told at some length on pp. 220–4.

About twenty different vitamins have already been recognised. In a sensible mixed diet they are all present in sufficient quantity, and in our own country, in normal times, there is seldom any need to concern ourselves with the question of vitamin deficiency.

We have been able to give only a few illustrations of the thousands of ways in which man has benefited by the work of the chemist. Whole books have been written on the subject. Let us remember once more, however, that chemistry is not to be regarded merely as a subject useful to the manufacturer of nitrates, fats, textiles, etc., or to the physician or surgeon, but as one which is worth studying for its own sake.

CHAPTER 1

A BRIEF REVIEW

Most likely you have already studied some of the simpler parts of Chemistry, and have acquired some ideas which will be extremely useful as you go more deeply into the subject. In this chapter we will make a brief review of certain parts of this earlier knowledge.

To begin with the term ***Chemistry*** itself, we may briefly define it as *the science which deals with the composition of matter* ('matter' being anything which has weight). Physics, too, deals with matter, but rather in its relation to the various forms of energy. For instance, if in Physics we are studying the subject of falling bodies, we think of the force of gravity and the kinetic energy acquired by the falling body, but are quite unconcerned with the composition of that body.

These terms 'chemical' and 'physical' are needed right at the beginning of our subject, as we speak of *chemical change* and *physical change.* It follows from the definition we have given of Chemistry that a chemical change is a change in the composition of a substance. We burn a piece of magnesium, for instance, and the silvery bright metal is converted into a dull white powder. Investigation shows that the powder still contains magnesium, but contains oxygen (derived from the air) as well, and because the powder differs in composition from the original magnesium, we say that a chemical change has taken place.

Now the 'analysis' of the white powder is a comparatively difficult task, but you must not conclude that an analysis is necessary before we can decide whether a chemical change has taken place. From mere observation we can feel pretty sure that the white powder is a different substance from the shining magnesium, and in such cases observation is usually sufficient. It would help us to decide, for instance, that the rusting of iron is a chemical change.

An example of a physical change would be that which takes place in a piece of platinum foil when held in a bunsen flame.

It has changed from a silvery colour to red, and of course from cold to hot—but it is still platinum. The changes are said to be physical because they do not involve a change in the composition of the substance. The melting of ice, and the conversion of water into steam, are other examples of physical changes.

Before leaving the subject let us consider a few other features of these two kinds of change.

(i) It is easily shown by experiment that the white powder, magnesium oxide, weighs more than the magnesium from which it was formed (the increase being derived from the oxygen of the air). On the other hand, when we heat platinum there is no change in weight, nor is there when we turn ice into water, or water into steam.

(ii) The chemical change magnesium→magnesium oxide is accompanied by the giving out of a great deal of heat, while the platinum when heated gives out only the heat it has previously received from the bunsen.

(iii) If we make a list of the properties of magnesium (colour, taste, density, melting point, etc.) and compare them with those of magnesium oxide, we find differences all along the line. On the other hand, in only a few respects do the properties of hot platinum differ from those of the cold metal.

(iv) It is not very easy to turn magnesium oxide back into magnesium. On the other hand, we can easily turn red-hot platinum into cold platinum, or steam into water, or water into ice. In short, a physical change is usually more easily reversed than a chemical one.

Let us summarise.

PHYSICAL CHANGE	CHEMICAL CHANGE
1. Substance remains the same.	A different substance is produced.
2. No change in weight.	Change in weight (at the cost of some other substance taking part).
3. Little or no heat given out (or taken in).	Much heat given out (or taken in).
4. Usually only a few of the properties are changed.	Complete change of properties.
5. Change is usually temporary and easily reversed.	Change is more permanent, and usually not so easy to reverse.

While the above comparison is broadly true, a few qualifications must be made. Mere *change of state* (solid to liquid, etc.) is certainly a physical change, for there is no change in the composition of the substance. Points 1, 2 and 5 apply perfectly, but some heat is certainly given out, or taken in. Thus heat must be *supplied* to turn ice into water, and considerable heat is *given out* when steam condenses. It would not be fair, either, to say that 'only a few of the properties are changed', for there is a wide difference between the properties of steam and those of ice. While we need not make too much of these deviations from general rules, we must not shut our eyes to them. The *essential* question is related to No. 1—Does the substance remain the same, or not? Nos. 2, 3, 4 and 5 may be regarded as convenient accompanying *signs*.

Elements, Compounds and Mixtures. Let us go back to the point that during a chemical change the substance concerned changes in weight. Slaked lime, for instance, if exposed to the action of carbon dioxide, changes into chalk, and in doing so becomes heavier. On the other hand, if slaked lime is strongly heated it changes into quicklime and becomes lighter.

But there are some substances which never undergo chemical change except with *increase* of weight. Magnesium, already mentioned, is an example. We can make it undergo many different chemical changes, but in every case the new substance formed weighs more than the original magnesium. Such substances are called ***elements***, and in fact we might define an element as *a substance which never undergoes chemical change except with increase of weight.* We can look at the matter in another way. Many substances when suitably treated (usually, but not always, under the action of heat) are *decomposed* into simpler substances, and it may be possible to decompose these further into still simpler ones. Before long, however, we arrive at substances which defy all efforts to decompose them—they are elements. They may undergo chemical change by *combining* with other elements, in which case we shall observe an increase of weight. But during a chemical change they are never *decomposed*, and so we never observe a decrease.

In all there are about a hundred elements. Some of them occur free in Nature (e.g. oxygen, nitrogen, gold), but most of them are found only in combination with other elements. Fig. 1/1 shows the extent to which some of the commonest elements are present in the earth's crust, but it should be mentioned that 'others' includes some very important elements—carbon, for instance, which though it occurs to the extent of only 0·2 per cent., is present in all living matter.

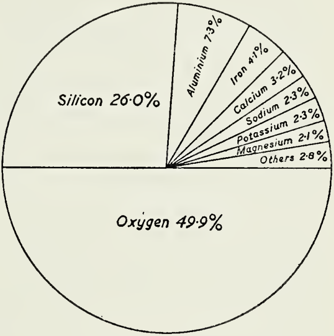


FIG. 1/1

We must next distinguish between *mixtures* and *compounds*; and here we can learn a great deal from a very old experiment with iron filings and flowers of sulphur. These are first thoroughly mixed and examined. We notice that

(i) The separate particles of iron and sulphur can be distinguished, lying side by side.

(ii) The two substances can be separated by mechanical means such as the action of a magnet, or by shaking up with water, when most of the sulphur comes to the top. If (as is usually the case) the particles of sulphur are finer than the others, we may separate the two by means of a sieve.

(iii) The colour and general appearance of the mixture is just about what we should expect—its properties are a sort of average of those of its constituents.

On heating the mixture it begins to burn. The bunsen may now be removed, and although no heat is now being supplied from outside, great heat is evidently being produced *within* the mass, for it glows with an intense fiery red colour.

After cooling, the mass is powdered up and examined. We find that

(i) The separate particles of iron and sulphur can no longer be distinguished, even if a powerful lens is used.

(ii) The methods we used before are no longer of any use to bring about a separation of the iron and sulphur. On shaking with water, the *whole* of it settles to the bottom. On applying a magnet, the *whole* of it is attracted.[1]

(iii) The colour and general appearance are no longer something between those of iron and sulphur.

The iron and sulphur have in fact disappeared as such, and a *new substance* has been formed. A substance so formed is known as a ***chemical compound.***

The essential difference between a compound and a mixture is that the very smallest particles of a compound are all alike, while in the case of a mixture they are not.

In the case of a powder, we can nearly always decide, perhaps with the help of a lens, whether we are dealing with a mixture or a compound. If a mixture, it may usually be separated into its components by what we may call 'selective solubility.' Take, for example, gunpowder, which is a mixture of nitre (soluble in water), sulphur (insoluble in water but soluble in carbon disulphide) and charcoal (soluble in neither of these liquids). We should first add water, heat and stir for a little while to dissolve the nitre, and then filter. On evaporating the clear filtrate to dryness we should obtain the nitre.

The residue on the filter-paper would be wet with nitre *solution.* To get it clear of nitre we should pour on successive quantities of hot water, and if we were required to recover *all* the nitre we should have to collect all the clear liquid filtering through, and evaporate it to dryness, along with the clear filtrate mentioned above.

The residue on the filter-paper is a mixture of charcoal and sulphur. We add successive quantities of carbon disulphide, collecting the filtrate in a large evaporating dish. This would be put in a fume cupboard and allowed to evaporate at room temperature (carbon disulphide vapour being very inflammable). The sulphur would be left in the dish, while the charcoal would, of course, remain on the filter-paper.

---

[1] If a magnet be applied again and again, it will attract a little each time until it has finally removed the whole. The fact that the magnetic properties of the compound are only feeble has frequently led to the conclusion that it is not magnetic at all.

Suppose we were required to separate some sandy sea-water into its three main constituents (i) sand, (ii) various soluble salts and (iii) water. We could filter and evaporate in an open dish, thus obtaining (i) and (ii), but in that case all the water would be lost. To obtain the water, we should have to do the boiling down in a distilling flask attached to a condenser (as in fig. 8/7 on p. 87), when pure water would distil over.

Ordinary 'water' is really a mixture of water and dissolved air. To separate the air from the mixture, we could drive it out by boiling, and collect it in the tube T (fig. 8/6 on p. 85).

The methods indicated above serve to separate many mixtures, but by no means all. Thus to separate a mixture of alcohol and water we employ a method known as *fractional distillation*, taking advantage of the fact that alcohol has a much lower boiling point (78°) than water (100°).[1] On distilling the mixture,[2] the alcohol (with some water) comes over first, but in this brief outline we cannot go into the question of how to obtain the alcohol completely free from water. In mixtures containing iron we should obviously make use of a magnet. In fact, in all cases we apply a treatment which has a different effect on the different constituents.

Solubility. In what has gone before, we have made reference to the fact that substances are frequently soluble in water. We must now go more thoroughly into this question of solubility.

It is easy to illustrate the fact that most substances dissolve more freely in hot water than in cold. If we put some nitre to a depth of about $\frac{1}{2}$ in. in a test-tube and cover it with cold water to a depth of 2 in., we shall find that however long we shake the mixture, some of the nitre remains undissolved. The cold water is *saturated* with nitre, and is unable to dissolve any more. On heating, however, the nitre soon disappears. Similar results are obtained with most other substances.

We shall now consider how to make more exact *measurements* of solubility, and it will therefore be necessary to say exactly what we mean by this term.

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[1] Unless otherwise stated it is to be understood that all temperatures mentioned in this book are *Centigrade*.

[2] Practical details are given on p. 23 of the author's *School Course of Practical Chemistry* (Bell).

The ***solubility*** *of a given substance in a given liquid, at a given temperature, means the number of grams of it which will dissolve in* 100 *gm.*[1] *of the liquid at the temperature considered, when an excess of undissolved substance is present.* The reason for adding the last eight words will appear later.

It is clear that a solution consists of two parts. The substance dissolved is often referred to as the ***solute,*** while the liquid in which it is dissolved is called the ***solvent.***

Solubility of Potassium Chlorate. Suppose we wish to find the solubility of potassium chlorate at a given temperature, say 30° C. We heat about 100 c.c. of water in a beaker to a slightly higher temperature, say 35° C., add powdered potassium chlorate and stir till it is completely dissolved. We now add more chlorate and keep repeating the process until even after much stirring, some powder remains undissolved at the bottom. Throughout this operation, the temperature must be kept up to 35° by an occasional touch of the bunsen.

We now allow the temperature to drop to 30°, stirring gently all the time with the thermometer. When the temperature of 30° is reached, a little of the solution is poured into a dry, weighed evaporating dish, care being taken not to disturb the undissolved powder at the bottom. The dish is now weighed again quickly (so that not much water shall be lost by evaporation), and the solution is afterwards evaporated to dryness. To avoid loss of the solid substance by spiriting, it is best to use a water-bath for the final stage of the evaporation.

When the water has been completely evaporated, the dish is allowed to cool and is afterwards weighed. The result is then worked out as in the following example :

(*a*) Weight of empty dish	25·38 gm.
(*b*) Dish + solution	51·42 ,,
(*c*) Dish + potassium chlorate (after evaporation)	28·27 ,,
Subtracting (*c*) from (*b*) we have	
Weight of *water*	23·15 ,,
Subtracting (*a*) from (*c*) we have	
Weight of *chlorate* dissolved by this water .	2·89 ,,

∴ at 30°, 23·15 gm. of water dissolves 2·89 gm. of chlorate.

∴ 100 gm. of water dissolves $\frac{2\cdot89}{23\cdot15} \times 100 = \mathbf{12\cdot48}$ gm.

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[1] Do not make the common mistake of saying 100 c.c.

Construction of a Solubility Curve. If we carried out a number of experiments like the one just described, but working at different temperatures, we should obtain results like the following for the solubility of potassium chlorate:

Temp. (° C.)	0	10	20	30	40	50	60	70	80	90	100
Solubility	3	5	7	10	14·5	20	26	32·5	39·5	47·5	56

Such results may be very neatly expressed by what is called a ***solubility curve.*** On a piece of squared paper temperature is marked off horizontally, using a scale of, say, $\frac{1}{2}$ in. to 10° C. The solubility is marked off vertically. Here 1 in. might represent 20 gm. The result is a curve such as that marked 'potassium chlorate' in the figure over-leaf.

A number of other solubility curves are shown in the same figure, and it is worth while to examine them for a few minutes.

In most cases, as the temperature rises, there is a rather rapid increase in the solubility. But notice the case of sodium chloride (common salt). From 0° to 100° the solubility increases only from 36 to 39, so that common salt is only slightly more soluble in boiling water than in water that is ice-cold.

Now look once more at the potassium chlorate curve. Suppose we took 100 gm. of water, heated it to 80° C., and saturated it with potassium chlorate at that temperature. We see by the curve that the water would dissolve 40 gm. What will happen if we now cool the water from 80° to 15° C.? (i.e. to about the temperature of the room). The curve shows us that at 15° C. the water can hold only 6 gm. of potassium chlorate in solution. The difference between these two amounts, i.e. 34 gm., will ***crystallise out*** as the solution is cooled.

It is very easy to illustrate the process of crystallising out.[1] Take a test-tube about one-third full of water. Heat the water nearly to boiling, and keep adding potassium chlorate until the water cannot dissolve any more (i.e. until it is saturated). Now cool the water under the tap. A big crop of

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[1] The subject receives fuller treatment on pp. 14–15 of the author's *School Course of Practical Chemistry* (Bell).

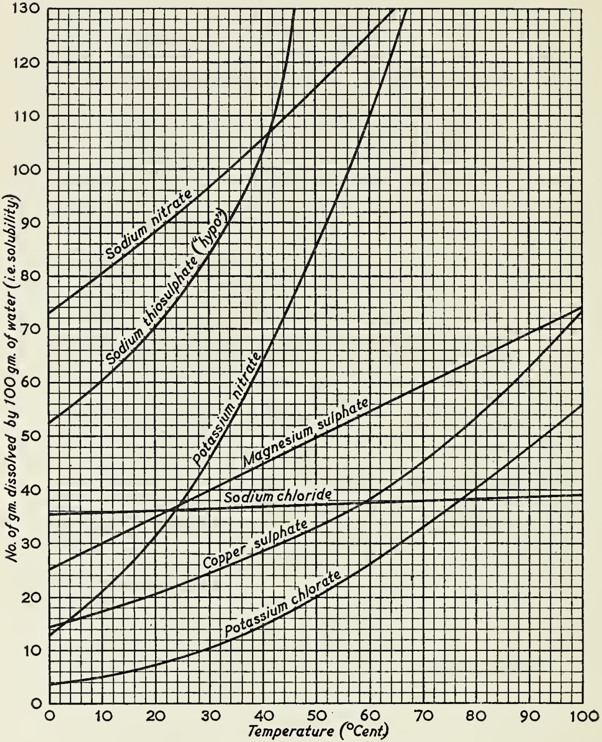

FIG. 1/2. Solubility curves

crystals is very quickly formed. Similar results may be obtained with nitre, lead chloride and scores of other substances.

Supersaturation. Suppose we saturate some water with 'hypo' at a temperature of say 40° C., and then filter the liquid into a clean flask containing a thermometer. Now let us put the liquid on one side to cool, a plug of cotton-wool being placed in the mouth of the flask to keep out particles of dust.

When the flask has cooled down to room temperature (say 15° C.) *no crystals are observed.* Yet, according to the curve, each 100 gm. of water saturated with hypo at 40° C. should give a deposit of $103 - 65 = 38$ gm. on cooling to 15° C.

Now let us drop ever such a little speck of hypo into the solution. We notice that a mass of crystals begins to form at once. The speck seems to act as a nucleus round which the process of crystallising can begin. Before this extra particle was added the liquid evidently contained in solution much more hypo than would correspond to the solubility curve. It would be said to be ***supersaturated.***

You can see now why in our solubility determination (p. 16) we took care to have *excess* of the potassium chlorate. This is not only a guarantee that the solution is saturated; it is also a guarantee that it is not *super*-saturated. You can see, too, why in our definition of solubility we included the condition that an excess of the undissolved substance must be present.

Other Solvents. It is often necessary to find a solvent for substances which are insoluble in water. Thus rubber is dissolved in petrol or benzene to make 'solution' for repairing punctures, etc. Spirit varnish is made by dissolving shellac in methylated spirit, and some kinds of lacquer by dissolving resin in turpentine. Tincture of iodine is described on p. 268. When removing stains from clothing we try to find a liquid in which the unwanted substance will dissolve. Thus tar stains are removed by rubbing with petrol; grease spots with benzene, petrol or carbon tetrachloride; paint spots with turpentine; and so on.

The alchemists believed in the existence of a universal solvent—the alkahest they called it—and spent much time searching for it. It is said that one of them announced triumphantly to some of his fellow-workers that he had at last found this universal solvent, but was completely at a loss when one of them asked the simple question 'What do you keep it in?'

Questions

N.B. Most of the questions in this book are reproduced from G.C.E. papers (at Ordinary Level) of the various examining bodies. To indicate the source, the following contractions will be used:

Brist. =*Bristol.*
Camb. =*Cambridge.*
Dur. =*Durham.*
J.M.B. =*Joint Matriculation Board (Northern Universities).*
Lond. =*London.*
O.C. =*Oxford and Cambridge Schools Examination Board.*
Oxf. =*Oxford.*
Scot.L.C. =*Scottish Leaving Certificate.*
W.J. =*Welsh Joint Education Committee.*

1. How can you distinguish between a *chemical* change and a *physical* change? What sort of change takes place when (*a*) sugar dissolves in water, (*b*) a match is struck, (*c*) ice melts, (*d*) a leaf decays, (*e*) an electric light is switched on?

2. Classify the following as elements, compounds or mixtures: chalk, mercury, gunpowder, gold, iron rust, graphite, rubber solution (for repairing punctures).

3. Define *the solubility of a salt in water.* Describe in detail how you would measure the solubility of sodium chloride in water at 25° C. The following results were obtained in experiments with copper sulphate:

Temp. (° C.)	0	10	20	30	40	50	60	70	80	90	100
Solubility	14·3	17·4	20·7	25·0	28·5	33·3	40·0	47·0	55·0	64·0	75·4

Draw the solubility graph for copper sulphate. *J.M.B.*

4. In what respects is the dissolving of common salt in water different from the 'dissolving' of zinc in hydrochloric acid?

When powdered black-board chalk is put into water it does not disappear. Describe in detail, an experiment by which you could find out whether any of it had, in fact, dissolved in the water.

How can you account for the use of (i) methylated spirit for making lacquers, (ii) petrol for cleaning clothes? *Camb.*

5. Construct the solubility curve of potassium nitrate from the following data:

At	0	10	20	30	40	60	70	80	90° C.
	13	21	32	46	64	110	138	169	204 gm.

of the salt are dissolved by 100 gm. of water.

From your curve find (*a*) the solubilities at 15° and 50° and (*b*) how much solid will crystallise out if 100 gm. of *solution*, saturated at 90°, are cooled from 90° to 20°.

6. The table shows the solubility of potassium chlorate in water (in grams substance per 100 gm. water) for various temperatures:

Temperature (° C.)	10	20	30	40	50	60	80
Solubility (gm./100 gm. water)	5·0	7·4	10·5	14·0	18·8	24·5	38·5

Draw the solubility curve, and use it to find (*a*) the solubility of potassium chlorate at 70° C., (*b*) the weight of potassium chlorate which will crystallise if 100 gm. of saturated solution at 55° C. are cooled to 15° C. *Camb.*

7. Solutions are said to be *unsaturated*, *saturated* or *supersaturated*: what does this mean?

Describe how you would prepare (*a*) a saturated solution of common salt at 40° C., (*b*) a supersaturated solution of sodium sulphate or some other suitable salt at room temperature. Briefly state how you would determine experimentally from (*a*) the solubility (in gm. solute per 100 gm. solvent) of common salt at 40° C.

Sketch the solubility graph of common salt for temperatures between 0° C. and 100° C. *Brist.*

CHAPTER 2

SOME FUNDAMENTAL LAWS

As you look at the title of this chapter you may feel that you are being plunged rather suddenly into a difficult part of the subject. However, as you read on you will probably find that these 'fundamental laws' are not very terrible, after all, though nobody is going to pretend that they are as easy or exciting as (say) Stevenson's *Treasure Island.* Of the three laws we shall deal with, the second and third bring us very quickly to Dalton's Atomic Theory, which is such a splendid foundation for all our future chemistry that there seems every reason for digging down to it as soon as we can.

So to begin with, what exactly is a 'law'?

By a 'law' in science we simply mean a general statement that sums up a number of isolated facts. Consider the following facts for instance:

(i) When phosphorus burns in air it gains in weight, but the air loses weight to an exactly equal extent.

(ii) Both lead nitrate and potassium iodide are white crystalline salts, easily soluble in water. When their solutions are mixed, there is a chemical change with the formation of a rather insoluble yellow substance, but the total weight after the chemical change is the same as the total weight before.

These isolated facts—and thousands more might be given—are summed up in the ***Law of Conservation of Mass***, which states that *Matter cannot be created or destroyed, though it may be changed from one form into another.*

We will now describe in a little more detail the experiments to which we have just referred.

To show that phosphorus gains in weight when burnt in air, we use the apparatus of fig. 2/1. The phosphorus, P, is contained in a glass tube containing some asbestos fibre, A, and connected with an aspirator, S. On slowly running water from the aspirator, a slow stream of air is drawn over the phosphorus, which is gently heated with a bunsen. The white fumes produced are stopped by the asbestos. If the tube containing the phosphorus is weighed before and then after the experiment, it will be found that there is a gain in weight.

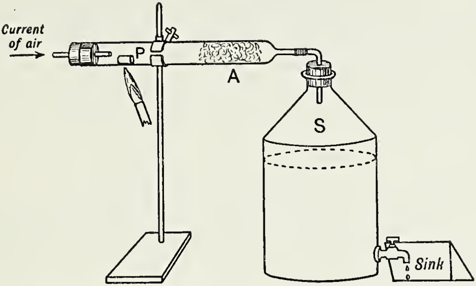

FIG. 2/1. Phosphorus gains in weight on burning

Let us now take a round-bottomed flask (say 400 c.c.), dry it carefully, and put a piece of dry phosphorus in it. We then fit it with a good rubber stopper and weigh it. (This is easily done by hanging it from the hook of the balance with a piece of cotton; cf. fig. 2/2.)

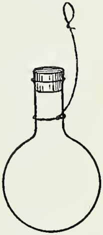

FIG. 2/2

On gently heating the phosphorus it takes fire. When it has finished burning we let the flask cool and then weigh it again. It weighs exactly the same as before.

Now the flask contains nothing but phosphorus and air. From the previous experiment we know that, on burning, the phosphorus has gained weight. Since the total weight (i.e. flask and contents) has not changed, *this gain of weight must have been at the expense of the air.*

The experiment with lead nitrate and potassium iodide is carried out as follows.

About 2 gm. of lead nitrate is dissolved in a little water in a conical flask fitted with a cork. The small test-tube contains about 2 gm. of potassium iodide dissolved in water. It is supported by a thread as shown in fig. 2/3, so that at this stage the two solutions do not mix. The complete apparatus is now weighed as exactly as possible.

Leaving the weights on the pan, the apparatus is now removed. The cork is raised for a moment to release the thread, and then replaced. The solutions mix, and a chemical change takes place with the production of a yellow precipitate of lead iodide. The apparatus is now put back on the scale-pan, and it is found that there is no change of weight.

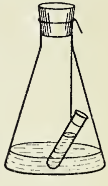

FIG. 2/3

Another very important law in chemistry is known as the ***Law of Definite Proportions***, or ***Law of Constant Composition***, which states that *a given chemical compound always has the same composition, no matter by what process it is made.* Here are two examples.

(i) Copper oxide obtained by heating copper in air or oxygen contains 79·9 per cent. of copper and 20·1 per cent. of oxygen.

Copper oxide obtained by heating either the nitrate or the carbonate has exactly the same composition.

(ii) Water made by the burning of hydrogen contains 11·1 per cent. of hydrogen and 88·9 per cent. of oxygen.

Water made by passing hydrogen over heated copper oxide has exactly the same composition; so also has pure rain-water.

Not all these 'isolated facts' lend themselves very readily to practical experiment, but it is quite easy to demonstrate most of them.

Experiments with Copper. When copper is heated in air it oxidises on the surface only, and the copper underneath is protected by the layer of oxide from further action. To prepare copper oxide in this way would therefore be tedious in the extreme, but we can soon prepare it by heating either the nitrate or the carbonate. Let us begin with the nitrate.

We put about 8 gm. of the pure nitrate in a dish, and heat it until brown fumes cease to be evolved. We cool it (in a desiccator if possible),[1] and weigh it. We now heat once more and weigh again. The object of this double weighing is to make sure that the change from nitrate to oxide is complete —if it is, the two weighings should, of course, agree. We have now prepared copper oxide from the nitrate, and in a quite similar way we can obtain it from the carbonate, only in this case no brown fumes are evolved—carbon dioxide comes off instead.

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[1] Copper oxide is *hygroscopic*, i.e. it absorbs moisture. See p. 86.

We now have to show that our two samples of copper oxide have the same composition. To do this, we can reduce them in a stream of hydrogen (or, more conveniently, coal-gas), using the apparatus shown in fig. 2/4. The porcelain boat A contains a weighed quantity of oxide derived from the nitrate, while B contains a weighed amount of the other specimen. The combustion-tube is heated,[1] and in a few minutes both specimens of oxide are reduced to copper.

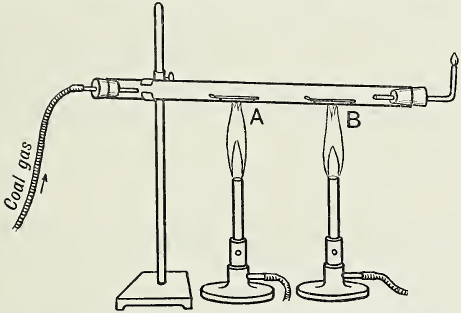

Fig. 2/4. Illustrating the Law of Constant Composition

Our results would be set out somewhat as follows:

		1st specimen	*2nd specimen*
(*a*) Wt. of porcelain boat		5·72	6·31
(*b*) Boat + oxide		7·97	8·16
(*c*) Boat + copper		7·52	7·79
∴ wt. of oxide, (*b*) − (*a*)	=	2·25	1·85
and wt. of copper, (*c*) − (*a*)	=	1·80	1·48
∴ percentage of copper in copper oxide	=	$\frac{1{\cdot}80}{2{\cdot}25} \times 100$	$\frac{1{\cdot}48}{1{\cdot}85} \times 100$
	=	80·0	80·0
and percentage of oxygen	=	20·0	20·0

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[1] The tube is given a slight downward slope from left to right, so that the water produced may not run back on the hot part and crack it.

Thus *the two specimens have precisely the same composition*, and so the law is illustrated.

Experiments with Water. Carefully dried hydrogen is passed through AB, a combustion-tube containing a considerable quantity of copper oxide.[1] The latter is heated, and the water produced passes (as vapour) into a series of calcium-chloride tubes, C, D, E . . .

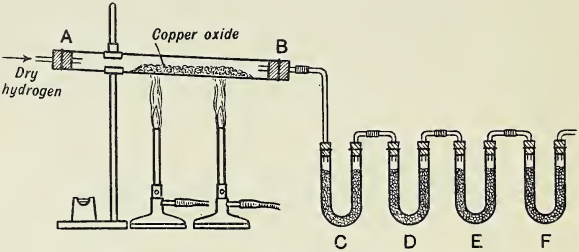

FIG. 2/5. Percentage composition of water

The tube AB, containing the copper oxide, is weighed before and after the experiment, and the loss of weight is the amount of oxygen removed from the copper oxide. Suppose this loss is 5·36 gm.

The tubes C, D, E . . . are also weighed before and after the experiment, and the *total* gain = wt. of water produced. Suppose this total gain is 6·03 gm.

We know that this 6·03 gm. of water contains 5·36 gm. of oxygen.

Therefore it contains 6·03 − 5·36 = 0·67 gm. of hydrogen.

From this point an easy calculation shows that water obtained in this way must contain 88·9 per cent. of oxygen and 11·1 per cent. of hydrogen.

N.B. The *last* of the series of drying tubes (F in the figure) should show no increase in weight at the close of the experiment. If it *does* increase in weight, we have no guarantee that all the moisture has been successfully absorbed.

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[1] See footnote on previous page.

Similarly, of the series of drying tubes attached to A (not shown in fig. 2/5), the one nearest to A should show no increase in weight. If it does, we have no guarantee that the hydrogen entering AB was dry.

We now have to show that pure rain-water has the same composition—oxygen 88·9 per cent. and hydrogen 11·1. The simplest plan is to add a small quantity of sulphuric acid[1] and submit the acidified water to electrolysis as described on p. 101. In this way we get the relative *volumes* of hydrogen and oxygen, and (knowing the weight of one litre of hydrogen and one litre of oxygen) it is then easy to calculate the relative weights and the percentage composition. It should agree exactly with that obtained in the previous experiment.

In volumetric work with burettes (Chapter 39) we often meet with examples of the Law of Constant Composition. Suppose, for instance, that we have a solution of sodium hydroxide and one of hydrochloric acid. We can measure very accurately the proportions in which these solutions neutralise one another (giving a solution of sodium chloride), and we find that if we increase or diminish the volume of sodium hydroxide we have to increase or diminish the volume of hydrochloric acid in exactly the same proportion. Thus the composition of the sodium chloride produced is constant.

We sometimes meet with *apparent* exceptions to this law. Bleaching powder, for instance, does not always contain the same percentage of chlorine, nor iron rust the same percentage of iron. The fact is that though bleaching powder consists mainly of a definite compound, calcium chloro-hypochlorite (p. 255), this is mixed with small quantities (varying from one sample to another) of other compounds such as calcium chloride and slaked lime. A similar explanation applies in the case of iron rust.

The composition of glass is very variable, but then glass is not a single compound—it is a mixture of compounds, usually silica and silicates. Ordinary solder is a mixture of tin and

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[1] It may be objected that we are no longer dealing with pure rain-water. It can be shown, however, that at the end of the experiment the same quantity of sulphuric acid is still present, so that for all practical purposes we may consider that only the water was decomposed.

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lead, and the higher the proportion of tin, the 'softer' the solder.

In short, apparent exceptions to the law are due in every case to the fact that we are dealing with a mixture, and not with a single compound.

We must now consider a third law.

It often happens that from the same two elements we can make two or more entirely different compounds. Thus we shall presently see that carbon and oxygen combine to form two quite distinct oxides, one of which (carbon dioxide) turns lime-water milky but does not burn, while the other (carbon monoxide) burns but does not affect lime-water. By suitable means—rather beyond the powers of the elementary student—it is possible to find the percentage of carbon and of oxygen in each of these oxides.[1] The results are expressed in the first two columns of figures.

	Carbon	*Oxygen*		*Carbon*	*Oxygen*
Carbon monoxide	42·86	57·14	*or*	1	1·33
Carbon dioxide	27·27	72·73	,,	1	2·66

There is nothing striking about the numbers in the first two columns. Let us now calculate what weight of oxygen combines with 1 gm. of carbon. In the case of the monoxide, 42·86 gm. of carbon combines with 57·14 gm. of oxygen. Therefore 1 gm. of carbon combines with $57{\cdot}14 \div 42{\cdot}86 = 1{\cdot}33$ gm. of oxygen. Similarly, in the case of the dioxide we find that 1 gm. of carbon combines with $72{\cdot}73 \div 27{\cdot}27 = 2{\cdot}66$ gm. of oxygen.

Now 2·66 is exactly twice 1·33. Is this a mere coincidence?

Let us take another case in which two given elements form more than one compound. Iron combines with chlorine, forming a colourless compound called ferrous chloride and a greeny-black one called ferric chloride. The percentage composition of these compounds is expressed in the first two columns of figures.

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[1] In the case of carbon dioxide, the method is as described on p. 163. Thus if 2·88 gm. of carbon gave 10·56 gm. of the dioxide, the percentage of carbon in carbon dioxide would be $\frac{2{\cdot}88}{10{\cdot}56} \times 100 = 27{\cdot}27$.

	Iron	*Chlorine*		*Iron*	*Chlorine*
Ferrous chloride	44·05	55·95	*or*	1	1·27
Ferric chloride	34·41	65·59	,,	1	1·91

In the third and fourth columns we have worked out, for each compound, the weight of chlorine which combines with 1 gm. of iron. These weights are 1·91 and 1·27. Now 1·91 is not twice 1·27, but *it is exactly* $1\frac{1}{2}$ *times* 1·27.

It looks as though we are on the track of a rather curious relationship. Let us take one more case. Lead forms several oxides, including a yellow one called litharge, and a brown one, lead dioxide. The results expressed as before would appear thus—

	Lead	*Oxygen*		*Lead*	*Oxygen*
Litharge	92·84	7·16	*or*	12·96	1
Lead dioxide	86·62	13·38	,,	6·48	1

Here, again, 12·96 is just twice 6·48.

Many more cases might be given. Let us sum up the essential points:

(i) All the cases under discussion are those in which two given elements form more than one compound.

(ii) The compounds are analysed, and their compositions are expressed in such a way that the weight of *one* of the components is the same in each.

(iii) It is then found that the weights of the *other* component are related to one another as small whole numbers, such as 2 : 1, 3 : 2, etc.

All these cases are summed up in the ***Law of Multiple Proportions***, which is conveniently stated as follows: *If two elements combine to form more than one compound, and the weight of one of the elements is the same in each, then the weights of the other element will be in a simple ratio to each other.*

The case of litharge and lead dioxide lends itself to easy experimental illustration.

2 gm. of litharge are weighed out into a porcelain boat, A, and 2 gm. of lead dioxide into another boat, B. The boats are placed in a combustion tube, CD, and the end C is joined to the gas-tap by a piece of bunsen tubing. The gas is lit at E—there should be enough gas to give a flame about

an inch high. The boats are now heated, and the oxides are soon reduced to lead by the hydrogen present in the coal-gas. As the hydrogen combines with the oxygen of the oxides, water is produced, and, as usual, the end D should be slightly lower than C so that this water may not run back on the hot part of the tube. A typical result would be as follows:

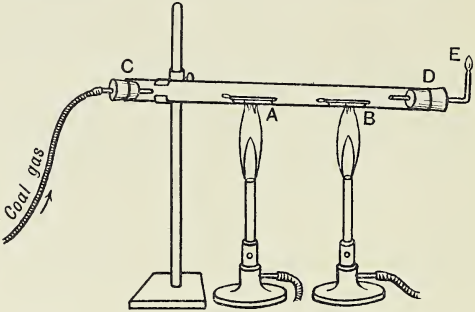

FIG. 2/6. Illustrating the Law of Multiple Proportions

	Litharge expt.	*Lead Dioxide expt.*
Wt. of porcelain boat	3·49 gm.	3·58 gm.
Boat + oxide	5·49 ,,	5·58 ,,
∴ wt. of oxide	2·00 ,,	2·00 ,,
Wt. of boat + lead (after expt.) . .	5·35 ,,	5·32 ,,
∴ wt. of lead (i.e. subtract wt. of boat) .	1·86 ,,	1·74 ,,
∴ wt. of oxygen	0·14 ,,	0·26 ,,
Wt. of lead combined with 1 gm. of oxygen	13·3 ,,	6·6 ,,

And 13·3 : 6·6 = 2 : 1 (approx.)

We will close by working out an example which illustrates much of what we have been discussing in the present chapter.

Three samples of oxides of copper were analysed with the following results:

(a) 6·21 *gm. contained* 4·96 *gm. copper.*

(b) 5·66 *gm. contained* 1·14 *gm. oxygen.*

(c) 7·05 *gm. contained* 6·26 *gm. copper.*

Work out (two decimal places) the weight of oxygen combined *with 10 gm. of copper in each sample, and point out any law, or laws, that are illustrated by your answers.*

The information supplied, and the weights of oxygen combined with 10 gm. of copper, are conveniently set out thus:

Sample	*Copper*	*Oxygen*	OR	*Copper*	*Oxygen*
(*a*)	4·96	1·25	(*a*)	10	2·52
(*b*)	4·52	1·14	(*b*)	10	2·52
(*c*)	6·26	0·79	(*c*)	10	1·26

It is clear from the answers obtained that we are concerned with *two different oxides* of copper (this is confirmed by the use of the word 'oxides' in the question as set).

(*a*) and (*b*) are samples of one of the oxides, and the answers illustrate the *Law of Constant Composition.*

Comparing with (*c*), where the numbers evidently refer to a different oxide, we notice that for a fixed weight of copper (10 gm.) the weight of oxygen in the one case (2·52 gm.) is exactly twice its weight in the other (1·26 gm.). Thus the *Law of Multiple Proportions* is illustrated.

On p. 27 we discussed the question of apparent exceptions to the Law of Constant Composition. Are there any exceptions, real or apparent, to that of Multiple Proportions? We will take up this point later (Chap. 19) when we shall be in a better position to discuss it.

Evidently the Law of Constant Proportions and the Law of Multiple Proportions are both concerned with the *weights* of elements which combine with one another to form compounds. Another important law, also dealing with weight relationships, is the Law of Reciprocal Proportions, but we will postpone this to Chapter 6.

Questions

1. State the Law of Conservation of Mass, and describe an experiment by which you could illustrate it.

2. A specimen *A* of copper oxide was prepared by heating copper carbonate, and a specimen *B* by heating the nitrate. Both were reduced to copper by heating in a stream of hydrogen.

It was found that 3·45 gm. of *A* yielded 2·76 gm. of copper, while 4·25 gm. of *B* yielded 3·40 gm. Show that we have here an illustration of the Law of Constant Composition.

3. 3·6 gm. of a certain metal, when burnt in oxygen, yielded 6·0 gm. of oxide. 3·0 gm. of the same metal, heated in steam, yielded 5·0 gm. of oxide. Show that these results illustrate the Law of Constant Composition.

4. 5 gm. of copper oxide, when heated in a current of hydrogen, gave 4 gm. of copper.

3 gm. of copper was, by suitable treatment, turned into copper oxide, and the latter was found to weigh 3·75 gm.

Show that these experiments illustrate the Law of Constant Composition.

5. When the hydrogen of the last question was passed over 5 gm. of copper oxide (leaving 4 gm. of copper) the water produced was collected and found to weigh 1·125 gm.

A quantity of water was electrolysed and found to yield 80 c.c. of hydrogen and 40 c.c. of oxygen (oxygen is sixteen times as heavy as an equal volume of hydrogen).

Show that these numbers illustrate the Law of Constant Composition.

6. 6·10 gm. of sodium, on heating in a current of chlorine, gave 15·5 gm. of sodium chloride.

4 gm. of sodium was turned into sodium hydroxide by the action of water. The sodium hydroxide, when neutralised with hydrochloric acid, gave 10·17 gm. of sodium chloride.

Show that these results illustrate the Law of Constant Composition.

7. Describe exactly, with a labelled sketch, how you would find the composition of water *by weight*. *Oxf.*

8. State the law of multiple proportions.

Weighed quantities of two oxides of the same metal were heated in a current of coal gas with the following results:

Weight of boat *A* empty = 4·500 gm.
Weight of boat *A* with first oxide before heating = 4·946 ,,
Weight of boat *A* with residue after final heating = 4·914 ,,
Weight of boat *B* empty = 5·000 ,,
Weight of boat *B* with second oxide before heating = 5·462 ,,
Weight of boat *B* with residue after final heating = 5·414 ,,

(*a*) Complete the calculation to show how the results are in accordance with the law of multiple proportions.

(*b*) Sketch the apparatus which would be used. *J.M.B.*

9. State the law of multiple proportions.

Analysis shows that two oxides *A* and *B* of the same metal contain 20% and 11·11% respectively of oxygen. Show that these figures agree with the law of multiple proportions.

Lond. (*part*)

10. State the Law of Multiple Proportions.

Give full practical details of an experiment you would make to verify the law in the case of the two oxides of copper.

A metal forms two chlorides which contain respectively 38·17 per cent. and 48·08 per cent. of chlorine. Find out if these results illustrate the above law. *W.J.*

11. State the Laws of Definite (Constant) and Multiple Proportions and show how Dalton's Atomic Theory explains them.

Nitric oxide and nitrogen dioxide contain respectively 46·7 per cent. and 30·4 per cent. of nitrogen by weight. Show that these two compounds illustrate the Law of Multiple Proportions. *Dur.*

12. Hydrogen was passed over 5 gm. of a certain oxide of lead (cf. p. 26) and the water produced was collected and found to weigh 0·404 gm. The experiment was repeated with 5 gm. of a different oxide of lead, and this time 0·753 gm. of water was obtained. Show that these numbers illustrate the Law of Multiple Proportions.

You may assume that water contains 8/9ths of its weight of oxygen, all of which is derived from the oxide of lead.

13. The black and red oxides of mercury contain 96·15 per cent. and 92·59 per cent. of mercury respectively. Show that this statement supports the Law of Multiple Proportions. *J.M.B.*

CHAPTER 3

THE ATOMIC THEORY

When a thing *always* happens, it is very natural to ask *why* it happens. Why *should* a given chemical compound always have the same composition? Why *should* there always be that curious 'simple ratio' that we observed in the Law of Multiple Proportions?

We cannot make much progress towards answering these questions unless we are prepared to think hard about *matter*—all the 'stuff' around us; everything that has weight, in fact. To begin with, we will deal with some matter that is an element, say lead.

Suppose we cut a bit of lead, say the size of a shilling, into halves; then into quarters, eighths, sixteenths, etc. How long could we continue the process?

'Until the bit of lead was too small to cut,' you answer. Suppose, however, there were absolutely no limit to the sharpness of our knife, and no limit to the keenness of our sight. Should we then be able to go on cutting for ever?

It may help us if we go in for a big-scale illustration. Imagine a huge giant about the size of Mount Everest amusing himself, not by cutting up a bit of lead, but by cutting Fleet Street into the smallest possible fragments. Everything about our giant is on the big scale—he finds it difficult, for instance, to make out any little specks smaller than St. Paul's Cathedral. We watch him at work. He has soon cut Fleet Street into separate buildings (beyond this stage he needs a magnifying glass), then he has cut the buildings into separate walls, and he goes on cutting and cutting—the mortar offering very little resistance—until he comes up dead against a real difficulty. *He has got down to the bricks.* To cut or pull bricks one from another is one thing; to divide a brick into parts may be quite another.

Is it not possible that our bit of lead may be made up of small parts just as Fleet Street is made up of bricks? Perhaps when we cut up the lead we are merely following the lines of the mortar, so to speak. The real lead 'bricks' may defy any attempt to divide them.

That, at any rate, was the view of John Dalton, who in 1808 put forward the 'Atomic Theory.' He suggested that any element such as lead might be made up of *atoms*. 'Atoms' comes from two Greek words, and means 'something that cannot be cut'; so it is a very suitable term. All the atoms of lead are exactly like one another, said Dalton. In particular, they all have the same weight. Another element, say sulphur, is also composed of its own special atoms, all exactly like one another, but unlike the atoms of lead or of any other element. There are as many different kinds of atoms as there are different kinds of elements.

There is reason to believe that the lightest atom is that of hydrogen, so we call its weight 1.[1] The oxygen atom is about sixteen times as heavy as the hydrogen atom, so we call its weight 16, and so on, the ***atomic weight*** of an element being *the weight of its atom when the weight of the hydrogen atom is taken as unity* (*one*). There is a table of atomic weights at the end of this book. Later on you will learn how some of them were obtained.

When two elements combine, Dalton said, the action that takes place is between the individual atoms. No doubt you remember heating iron filings and sulphur. The mass became fiery red. We must think of each individual atom of iron combining with an individual atom of sulphur. We now have what Dalton called 'compound atoms' (the modern term is 'molecules'), each containing one atom of iron and one of sulphur. If there are more sulphur atoms than iron atoms, the surplus sulphur atoms will just remain uncombined, and similarly if there are surplus iron atoms. Let us suppose we have removed the surplus sulphur or iron as the case may be, leaving pure iron sulphide. This is represented in fig. 3/1, each black circle representing an iron atom and each white circle a sulphur atom.

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[1] Strictly speaking, the atomic weight of oxygen (16) is taken as the basis, and the atomic weight of hydrogen then comes out to 1·008. However, this point may very well be left for the present, and is only mentioned here because otherwise the student might wonder why the atomic weight of hydrogen is given in the table as 1·008.

This figure represents 10 *molecules* of iron sulphide. Let us consider the composition of this substance—the proportion of iron it contains and the proportion of sulphur.

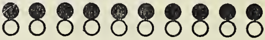

Fig. 3/1

As each iron atom weighs x units and each sulphur atom y (where x and y are the respective atomic weights) it is evident that *in a single molecule*

$$\text{wt. of iron} : \text{wt. of sulphur} = x : y$$

In the 10 molecules of fig. 3/1

$$\text{wt. of iron} : \text{wt. of sulphur} = 10x : 10y = x : y$$

Now a quantity of iron sulphide large enough to handle would have to be represented not by 10 double circles but by countless millions of them. Suppose this enormous number is n. Then total weight of iron is nx and total weight of sulphur is ny.

$$\therefore \text{wt. of iron} : \text{wt. of sulphur} = nx : ny = x : y$$

It is clear that whether we consider 1 molecule, or 10 or n (where n may be as large as we like), the ratio wt. of iron : wt. of sulphur is always the same ($= x : y$). In other words, iron sulphide will always have the same composition.

Thus, if we accept Dalton's theory, the Law of Constant Composition follows as a necessary consequence.

Let us next consider what would happen if each iron atom combined with *two* sulphur atoms forming a quite different compound of iron and sulphur. We can represent it thus:

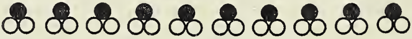

Fig. 3/2

In n such molecules we should have total weight of iron $= nx$
and total weight of sulphur $= n \times 2y$

$$\begin{aligned}\therefore \text{wt. of iron} : \text{wt. of sulphur} &= nx : 2ny \\ &= x : 2y\end{aligned}$$

Now in the first iron + sulphur compound, for every x gm. of iron we had y gm. of sulphur. In the second one, for every x gm. of iron we have $2y$ gm. of sulphur. It is clear that, arguing from Dalton's theory as a basis, we have arrived at the Law of Multiple Proportions!

In the same sort of way it can be shown that the Law of Reciprocal Proportions (discussed in Chapter 6) follows as a third consequence of the Atomic Theory. Summing up, we may say that the case stands something like this. We cannot *directly* verify the Atomic Theory.[1] But arguing from it as a starting-point, we are led to three important laws which stand the test of experiment, and therefore we believe the theory to be true.

It may be formally stated as follows:

(*a*) Every element consists of atoms which for any given element are all alike; in particular, they are alike as regards weight.

(*b*) When elements A and B combine, the combination takes place between their atoms.

(*c*) This combination takes place in *simple numerical ratios* of the atoms concerned, e.g. 1 atom of A + 1 atom of B; 1 atom of A + 2 atoms of B; 2 atoms of A + 1 atom of B; 3 atoms of A + 2 atoms of B, etc.

Notice that the 'simple ratio' which we observed in the Law of Multiple Proportions depends on the simple ratio in which the *atoms* of A and B are supposed to combine.

In the next chapter we shall see how the Atomic Theory helps us to obtain a clear idea of all sorts of chemical changes. We will conclude this one with a few particulars of John Dalton, to whom, as we have seen, the theory is due.

He was of Quaker stock, and was born at the small village of Eaglesfield in Cumberland in the year 1766. Considering his poor circumstances and the times in which he lived he received a very fair education, and he was specially interested in mathematics. He seems to have been persevering rather than brilliant. We read, for instance, that if his teacher had set him a rather harder exercise than usual and asked him later on if he had done it, he would answer, 'No, I can't deu't to-neet, but mebbe i' th' morn I will.' And 'i' th' morn' he would usually produce the solution. He was a 'sticker.'

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[1] This is no longer quite true. During recent years much of Dalton's theory may be said to have been directly verified, while some of it has been shown to require modification. See pp. 502–512.

Throughout his life we can trace these same features that were evident in his boyhood—i.e. he was always interested in *quantities*, in the *mathematical* side of things, and he arrived at his great theories not by quick, brilliant thinking so much as by long-continued deep reflection accompanied by experimental work. There is ample evidence, for instance, that the Atomic Theory grew up in his mind very slowly.

His work on the Atomic Theory made him very famous, but did not spoil him. One day the French chemist, M. Pelletier, came specially from Paris to Manchester to see him. At the moment, Dalton was helping a pupil with arithmetic. 'Est-ce que j'ai l'honneur de m'adresser à Monsieur Dalton?' said M. Pelletier. Dalton was not at all flustered, but just answered, 'Yes. Wilt thou sit down whilst I put this lad right about his arithmetic?'

He died in 1844 at the age of seventy-seven. With the establishment of the Atomic Theory in 1808, following on the overthrow of the Phlogistic Theory (say 1783), chemistry was now in a position to make very rapid progress.

Questions

1. What do you understand by the terms *atom, atomic weight, molecule*?

2. Give some account of the Atomic Theory. In what way are the laws of Constant Composition and Multiple Proportions connected with it?

3. The atomic weight of lead is 207 and of oxygen is 16. When one atom of lead combines with one of oxygen a molecule of 'litharge' is produced. In one such molecule the ratio wt. of oxygen : wt. of lead is obviously 16 : 207.

In ten such molecules, what would be (i) the total weight of oxygen, (ii) the total weight of lead, (iii) the ratio wt. of oxygen : wt. of lead?

Answer the same question taking the case of n molecules.

4. One atom of lead may combine with *two* atoms of oxygen forming a molecule of 'lead peroxide.'

What would be the weight of oxygen, weight of lead, and the ratio wt. of oxygen : wt. of lead in (i) 1 molecule of lead peroxide, (ii) 10 molecules, (iii) n molecules?

5. Compare the ratio obtained in Question 4 with that obtained in Question 3. For a fixed weight of lead, what do you notice about the two weights of oxygen? What law is thus illustrated?

6. What do you know of John Dalton?

7. Write a short essay on 'Why we regard matter as consisting of atoms and molecules?' *Oxf.*

CHAPTER 4

FORMULÆ AND EQUATIONS

Dalton used a distinct 'symbol' for each element. Thus he wrote ○ for oxygen, ⊙ for hydrogen, ⦶ for nitrogen, etc. Note that, strictly speaking, ○ stands for one *atom* of oxygen, ⊙ for one *atom* of hydrogen, etc. A 'compound atom' was denoted by writing the separate symbols side by side, e.g. Ⓘ ⊕ stood for a 'compound atom,' or 'molecule,' as we should now call it, of iron sulphide. The fact that iron combines with sulphur, forming iron sulphide, was represented by an *equation* thus:—

Ⓘ + ⊕ = Ⓘ ⊕

i.e. one atom of iron combines with one atom of sulphur, forming one molecule of iron sulphide.

Berzelius suggested that it would be much simpler to use the initial letter of the element as symbol—O for oxygen, H for hydrogen, N for nitrogen, etc. When two or more elements began with the same letter (e.g. carbon, calcium, chlorine, etc.), a second *small* letter was added to distinguish. Thus

C stands for one atom of carbon
Ca ,, ,, ,, calcium
Cl ,, ,, ,, chlorine, etc.

In some cases the letter (or letters) are taken from the Latin name instead of from the English one, e.g. K for one atom of potassium (kalium), Na for one atom of sodium (natrium), etc.

Berzelius's system is evidently much simpler than Dalton's, and it soon came into general use. Dalton, however, seems to have been very fond of his little circles, and as late as 1837, in a letter to Graham, he writes: 'Berzelius's symbols are horrifying.' He goes on to suggest that they are as hard to understand as letters of the Hebrew alphabet—which is just about what other people had thought of *his*!

Using Berzelius's symbols, the combination of iron with sulphur would be represented by the equation $Fe + S = FeS$.

Just as we speak of S as being the *symbol* of the element sulphur, we say that FeS is the *formula* of the compound iron sulphide. A formula shows what kind of atoms, and how many of each, are present in one molecule of a given compound. Thus when we say that the formula of sulphuric acid is H_2SO_4, we mean that one molecule of sulphuric acid contains two atoms of hydrogen, one of sulphur, and four of oxygen.

Molecules. So far we have used the term 'molecule' as being equivalent to Dalton's 'compound atom.' 'Molecule,' however, is a wider term than compound atom.

A ***molecule*** *is the smallest portion of a substance that can occur in the free condition.* The molecule of iron sulphide consists of one atom of iron combined with one of sulphur, and here 'molecule' and 'compound atom' mean the same thing. The smallest portion of mercury, however, that can occur in the free condition happens to be a single atom. Hence a molecule of mercury is in this case the same as an atom of mercury. There is definite evidence (which we shall consider in Chapter 11) that the smallest portion of hydrogen that can occur in the free condition consists of two atoms combined with one another. We express this by writing H_2 (*not* 2H, which would mean two atoms of hydrogen not combined with one another).

If you find this point rather puzzling, think of a man who sells scissors, and suppose he represents each *blade* by the symbol S, and a *pair* of scissors by S_2. Then $2S_2$ would stand for two pairs, $3S_2$ for three pairs and so on. 2S would stand for two *separate blades*, and in the ordinary way the man does not deal in such things. In any case, '2S' would have *quite different properties from* S_2—the properties of two separate daggers rather than of a pair of scissors.

In the same way, nature in the ordinary way does not deal in '2H,' and two separate atoms of hydrogen would have *quite different properties* from those of a molecule (H_2). Remember then that H (and similarly O, Cl, N) is just about as unusual as a 'scissor.'

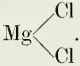
But while 'S_2' is the unit for selling purposes, 'S' is certainly the unit in the factory. When the workman is making changes such as fitting a new blade, he deals with 'S'—and so nature deals with 'H' in her chemical changes. In fact, an ***atom*** may be conveniently defined as *the smallest portion of an element which can take part in a chemical change.*

Valency. We shall make much more rapid progress in the writing of equations if we try to get some clear ideas on what is called 'valency.' Water has the formula H_2O, i.e. its molecule consists of one atom of oxygen combined with two of hydrogen. Oxygen is therefore said to have a *valency* of 2, by which we mean that an atom of oxygen combines with two atoms of hydrogen. Again, the hydrogen in water may be *displaced* by magnesium, one atom of magnesium displacing two atoms of hydrogen. Instead of H_2O we then have MgO. Magnesium is said to have a valency of 2, because one atom of this element displaces two atoms of hydrogen. *The* ***valency*** *of an element is the number of atoms of hydrogen which one atom of that element will combine with or displace.*

A little later (p. 238) we shall meet with a substance called hydrogen chloride. The molecule of this substance consists of one atom of hydrogen combined with one atom of chlorine, i.e. the formula is HCl. Clearly the valency of chlorine is *one*. It is often convenient to use chlorine as a sort of standard instead of hydrogen. Thus the formula for sodium chloride is $NaCl$, and we say that the valency of sodium is one because an atom of sodium combines with one atom of *chlorine*. Potassium (K) and silver (Ag) have also a valency of one, their chlorides having the formulæ KCl and $AgCl$. It is worth while remembering that sodium, potassium and silver have a valency of one, and that most of the other common metals have a valency of two. Thus magnesium chloride, for instance, would have the formula $MgCl_2$.

Notice that if two elements X and Y have the same valency (two, for instance), then if they combine with one another they will do so 'on equal terms' so to speak. Thus iron has a valency of two (iron chloride is $FeCl_2$), and so has sulphur (hydrogen sulphide is H_2S). Therefore iron sulphide is FeS.

In the same way, most *oxides* of metals have the formula MO, where M is the symbol of the metal. This simple formula is due to the fact that the valency of most of the common metals is the same as that of oxygen, i.e. two. Thus the formula of zinc oxide is ZnO, of mercuric oxide HgO, of copper oxide CuO and so on.

It is evident that valency somehow stands for *combining power*. Thus the formulæ $MgCl_2$ and $NaCl$ remind us that an atom of magnesium has the power of combining with two atoms of chlorine, while an atom of sodium is able to combine only with one. Hence the valency is often indicated by straight lines called 'bonds' or 'links,' such as —Mg— (or Mg=), Na—, etc. When magnesium combines with chlorine, the links from the magnesium are supposed to be engaged with those from the chlorine, thus  . Sodium chloride would be Na—Cl. Notice that when two elements combine, the number of links must be the same for each element, so that the lower the valency, the larger must be the number of atoms. In fact, the product

(*number of atoms*) × (*valency*) is the same for each, e.g.

(1) *Magnesium chloride*, $MgCl_2$

No. of atoms of Mg = 1. Valency of Mg = 2. Product 1 × 2 = 2.
,, ,, Cl = 2. ,, ,, Cl = 1. ,, 2 × 1 = 2.

(2) *Phosphorus pentoxide*, P_2O_5

No. of atoms of P = 2. Valency of P = 5. Product 2 × 5 = 10.
,, ,, O = 5. ,, ,, O = 2. ,, 5 × 2 = 10.

Terms Used. Instead of saying that an element has a valency of one, we often say that it is *univalent*. Similarly, elements with a valency of two, three, four and five are said to be *divalent*, *trivalent*, *quadrivalent* and *quinquevalent* respectively. Unfortunately, another set of terms is in use, and elements are said to be *monovalent*, *bivalent*, *tervalent*, *tetravalent* and *pentavalent*. We shall generally use the former set of terms in this book, but it is necessary to be familiar with the others because they are quite often met with.[1]

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[1] For some account of the electrical character of valency, see pp. 507–9.

In your earlier work you must have met with a large number of chemical changes, produced by the heating of elements in oxygen, the action of sulphuric acid on zinc, the heating of chalk and by many other experiments that you have carried out. We shall now refer again to some of these, giving the equation, with explanations where necessary.

In spite of the rather alarming appearance of the remainder of the chapter, you are strongly advised to work steadily through it. You will find that your work in chemistry becomes much easier when you have once grasped the idea of equations. For the same reason you should try to work through most of the questions at the end of the chapter.

People who 'never *could* make much of chemistry' are usually those who failed to get hold of this part of the work.

Burning magnesium in oxygen

$$2Mg + O_2 = 2MgO$$

Note. A simpler equation would be $Mg + O = MgO$. But the smallest quantity of oxygen which occurs in the free condition (the 'molecule,' p. 41) consists of two atoms, written O_2. To combine with this, two atoms of magnesium are required. We write 2Mg, not Mg_2, because we simply do not know how many atoms there are in the molecule of solid magnesium, and so we may as well take the simplest number, 1.

$$2MgO \text{ is short for } MgO + MgO$$

Burning zinc and calcium in oxygen

$$2Zn + O_2 = 2ZnO \quad \text{and} \quad 2Ca + O_2 = 2CaO$$

These cases are similar to the one just discussed.

Burning carbon and sulphur in oxygen

$$C + O_2 = CO_2$$
$$S + O_2 = SO_2$$

Note that the valency of carbon is *four*, for the two atoms of oxygen with which it combines would themselves combine with four atoms of hydrogen.

Similarly (in this case) for sulphur.

Phosphorus burning in oxygen

$$P_4 + 5O_2 = 2P_2O_5$$

P_4—not 4P—because the molecule of phosphorus consists of four atoms; a rather unusual case. The compound is known as phosphorus pentoxide.

Sodium burning in oxygen

$$2Na + O_2 = Na_2O_2$$

Na_2O_2 contains more oxygen than we should have expected (sodium being univalent), and is therefore known as sodium *peroxide* (p. 145). Sodium *oxide* (Na_2O) may be produced, however, by gently heating sodium in a limited supply of oxygen.

$$[2Na + O = Na_2O] \qquad 4Na + O_2 = 2Na_2O$$

The equation given in square brackets is incorrect, because the molecule of oxygen consists of *two* atoms, as already explained. In such cases we shall in future often give the simpler equation in square brackets, as here, and write the correct equation afterwards.

Acids formed when the oxide of a non-metal combines with water

$$\underset{\textit{Carbon dioxide}}{CO_2} + H_2O = \underset{\textit{Carbonic acid}}{H_2CO_3}$$

$$\underset{\textit{Sulphur dioxide}}{SO_2} + H_2O = \underset{\textit{Sulphurous acid}}{H_2SO_3}$$

$$\underset{\textit{Phosphorus pentoxide}}{P_2O_5} + H_2O = \underset{\textit{Metaphosphoric acid}}{2HPO_3}$$

Action of water on basic oxides

$$\underset{\textit{Sodium oxide}}{Na_2O} + H_2O = \underset{\substack{\textit{Sodium hydroxide} \\ \text{(`}\textit{caustic soda}\text{')}}}{2NaOH}$$

$$\underset{\textit{Calcium oxide}}{CaO} + H_2O = \underset{\textit{Calcium hydroxide}}{Ca(OH)_2}$$

Note that though oxygen has a valency of two and hydrogen a valency of one, the 'hydroxide' group OH has a valency of *one* only, not three. This is because one of the two oxygen 'links' is engaged with the hydrogen link, and only one link is free, thus —O— —H, written —OH for short.

Action of basic oxide on acid

CaO	+	H_2CO_3	=	$CaCO_3$	+	H_2O
Calcium oxide		*Carbonic acid*		*Calcium carbonate* (*a 'salt'*)		*Water*

Making mercuric oxide

$$[Hg + O = HgO]$$
$$2Hg + O_2 = 2HgO$$

(Two *separate* atoms of mercury, but two *combined* atoms of oxygen.)

Questions

1. What is meant by the terms *symbol* and *formula*? Who invented our system of chemical symbols? Give some account of the system, and of the older one which it displaced.

2. Give the formula for the following compounds: Magnesium oxide, mercuric oxide, carbon dioxide, sulphur dioxide, water, carbon monoxide, sulphuric acid, hydrochloric acid, carbonic acid.

3. Define the terms *atom*, *molecule* and *valency*.

4. Give the valency of each element other than hydrogen in the following compounds: Water (H_2O), methane (CH_4), ammonia (NH_3), hydrogen chloride (HCl).

5. Assuming that oxygen is divalent, what is the valency of zinc in zinc oxide (ZnO), of sodium in sodium oxide (Na_2O), of iron in ferric oxide (Fe_2O_3), of phosphorus in phosphorus pentoxide (P_2O_5) and of carbon in carbon dioxide (CO_2)?

Why do we assume that oxygen is divalent?

6. What is wrong with the following equations?

(i) $Mg + O = MgO$

(ii) $CO_2 + Ca(OH)_2 = CaCO_3 + 2H_2O$

(iii) $Zn + H_2SO_4 = ZnSO_4 + 2H$

(iv) $KClO_3 = KCl + O_3$
Potassium chlorate *Potassium chloride*

(v) $CaCO_3 + HCl = CaCl_2 + H_2O + CO_2$

7. Complete the following equations:

(i) $C + O_2 =$

(ii) $CO_2 + H_2O =$

(iii) $SO_2 + H_2O =$

(iv) $2Hg + O_2 =$

(v) $2Na + 2H_2O =$

(vi) $CaCO_3 = CaO +$

(vii) $CO_2 + Ca(OH)_2 = CaCO_3 +$

(viii) $CO_2 + 2Mg = 2MgO +$

8. Express the following statements in the form of equations:

(i) Magnesium burns in oxygen, forming magnesium oxide.

(ii) When mercuric oxide is heated, it decomposes into mercury and oxygen.

(iii) Sulphur burns in oxygen, forming sulphur dioxide.

(iv) When carbonic acid (H_2CO_3) is heated, it decomposes into water and carbon dioxide.

(v) When water is added to calcium oxide, calcium hydroxide is produced.

(vi) When carbon dioxide is passed over strongly heated carbon, carbon monoxide is produced.

CHAPTER 5

CALCULATIONS, CHIEFLY ON THE RELATION BETWEEN FORMULA AND PERCENTAGE COMPOSITION

In the last chapter we saw that, by means of equations, we could very conveniently summarise all sorts of chemical reactions. In our equation we mention (by their formulæ) all the substances that take part in the chemical change, and all the new substances that are produced.

By taking account of atomic weights we can go much further—we can make an equation give us exact information about the *quantities* concerned. With such information, the chemical manufacturer, for instance, knows exactly how much of this or that raw material he must order, and he can readily tell whether a given process is wasteful, or whether it is giving him the full 'theoretical' yield. Of course the scientist as well as the manufacturer is concerned with the measurement of quantities, and in the present short chapter we shall gain some idea of how both of them make their calculations. It will be best to work through a few typical examples.

1. *Calculate the percentage of oxygen in mercuric oxide, HgO.* [*Hg* = 200, *O* = 16.]

N.B. The numbers in brackets always indicate atomic weights.

One molecule of mercuric oxide, HgO, weighs $200 + 16 = 216$ units (the 'unit' being the weight of one atom of hydrogen).

The atom of oxygen in one molecule of mercuric oxide weighs 16 units.

$$\therefore \text{ percentage of oxygen } \textit{in one molecule} = \frac{16}{216} \times 100 = \mathbf{7{\cdot}41}.$$

Now a quantity of mercuric oxide is made up of a large number of similar molecules. One molecule is therefore a fair sample of the whole quantity, and so the percentage of oxygen in one molecule (7·41) is also the percentage in any quantity.

In future calculations we shall assume this principle (i.e. that a molecule is a fair sample of the whole quantity) without expressly stating it.

2. *Calculate the percentage composition of potassium chlorate* $KClO_3$. $[K=39,\ Cl=35{\cdot}5,\ O=16.]$

K	39
Cl	35·5
$O_3 = (3 \times 16)$	48
$KClO_3$	122·5

122·5 parts by weight of potassium chlorate contain 39 parts by weight of potassium.

$$\therefore \text{ percentage of potassium} = \frac{39}{122{\cdot}5} \times 100 = 31{\cdot}8.$$

Similarly, percentage of chlorine $= \dfrac{35{\cdot}5}{122{\cdot}5} \times 100 = 29{\cdot}0$, and percentage of oxygen $= \dfrac{48}{122{\cdot}5} \times 100 = 39{\cdot}2$.

Thus potassium chlorate contains ***31·8 per cent. of potassium, 29·0 per cent. of chlorine,*** and ***39·2 per cent. of oxygen.*** The three quantities add up to 100, as we should expect.

3. *Calculate the percentage of water of crystallisation in hydrated copper sulphate,* $CuSO_4.5H_2O$. $[Cu=64,\ S=32,\ O=16,\ H=1.]$

Cu	64
S	32
$O_4 = (4 \times 16)$	64
$5H_2O = 5(2+16)$	90
$CuSO_4.5H_2O$	250

Hence the complete molecule weights 250 units, and the water of crystallisation contained in it weighs 90 units.

$$\therefore \text{ required percentage} = \frac{90}{250} \times 100 = \boldsymbol{36}.$$

4. *Find the simplest formula of a compound which consists of potassium* 31·8 *per cent., chlorine* 29·0 *per cent., and oxygen* 39·2 *per cent.* $[K=39,\ Cl=35{\cdot}5,\ O=16.]$

Instead of expressing the composition by the numbers 31·8, 29·0 and 39·2, we may evidently express it by *any* numbers in which the same proportion is maintained.

Accordingly, change 31·8 to 39 (atomic weight of potassium) and change the other numbers in proportion. To do this we multiply each number by $\frac{39}{31 \cdot 8}$, so that

$$\begin{array}{llll} \text{Potassium} & 31 \cdot 8 & \text{becomes} & 31 \cdot 8 \times \frac{39}{31 \cdot 8} = 39 \\ \text{Chlorine} & 29 \cdot 0 & ,, & 29 \cdot 0 \times \frac{39}{31 \cdot 8} = 35 \cdot 6 \\ \text{Oxygen} & 39 \cdot 2 & ,, & 39 \cdot 2 \times \frac{39}{31 \cdot 8} = 48 \cdot 1. \end{array}$$

The 'parts by weight' may be expressed in any units we choose—grams, tons, ounces, etc. Let us choose *chemical* units (i.e. where 1 is the weight of the hydrogen atom). Then

39·0	parts by weight	represent	1	atom	of potassium
35·6	,,	,,	1	,,	chlorine
48·1	,,	,,	3	atoms	of oxygen

The simplest formula is therefore $\boldsymbol{KClO_3}$

N.B. (i) 'Simplest' formula[1] because formulæ such as $K_2Cl_2O_6$, $K_3Cl_3O_9$, etc., would have agreed equally well with the given information.

(ii) For clearness the above working has been shown at considerable length. The following statement, however, would be considered sufficient in the ordinary working of the problem

Elements	*Percentage*	*These numbers are proportional to*	*If* 1 = H
Potassium	31·8	$31 \cdot 8 \times \frac{39}{31 \cdot 8} = 39$	39 = K
Chlorine	29·0	$29 \cdot 0 \times \frac{39}{31 \cdot 8} = 35 \cdot 6$	35·6 = Cl (nearly)
Oxygen	39·2	$39 \cdot 2 \times \frac{39}{31 \cdot 8} = 48 \cdot 1$	48·1 = 3O (nearly)

∴ simplest formula is $\boldsymbol{KClO_3}$

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[1] Instead of 'simplest formula,' the term 'empirical formula' is often met with.

5. *Find the simplest formula of a compound which consists of iron* 70 *per cent. and oxygen* 30 *per cent.* [$Fe = 56$, $O = 16$.]

Arranging as above, we have

Elements	*Percentage*	*These numbers are proportional to*	*If* 1 = H
Iron	70	$70 \times \frac{56}{70} = 56$	56 = Fe
Oxygen	30	$30 \times \frac{56}{70} = 24$	$24 = 1\frac{1}{2}O$

N.B. Our calculation leads in the first place to the result $FeO_{1\frac{1}{2}}$, but, of course, we must have whole numbers of atoms.

The simplest possible formula is therefore $\boldsymbol{Fe_2O_3}$

6. *Find the simplest formula of a compound having the percentage composition iron* 20·1, *sulphur* 11·5, *oxygen* 23·0, *water of crystallisation* 45·4. [$Fe = 56$, $S = 32$, $O = 16$.]

Elements, etc.	*Percentage*	*These numbers are proportional to*	*If* 1 = H
Iron	20·1	$20{\cdot}1 \times \frac{56}{20{\cdot}1} = 56{\cdot}0$	56·0 = Fe
Sulphur	11·5	$11{\cdot}5 \times \frac{56}{20{\cdot}1} = 32{\cdot}0$	32·0 = S
Oxygen	23·0	$23{\cdot}0 \times \frac{56}{20{\cdot}1} = 64{\cdot}1$	64·1 = 4O
Water	45·4	$45{\cdot}4 \times \frac{56}{20{\cdot}1} = 126{\cdot}5$	$126{\cdot}5 = 7H_2O$

∴ simplest formula is $\boldsymbol{FeSO_4.7H_2O}$

7. 7 *gm. of a metal X (atomic weight* 56) *is converted into a hydrated sulphate. This is found to weigh* 35·1 *gm. and to contain* 28·8 *per cent water of hydration. Find the simplest formula of the hydrated sulphate.* ($H = 1$, $O = 16$, $S = 32$.)

Wt. of water of hydration $= \frac{28{\cdot}8}{100} \times 35{\cdot}1 = 10{\cdot}1$ gm.

∴ Wt. of anhydrous sulphate $= 35{\cdot}1 - 10{\cdot}1 = 25{\cdot}0$ gm.

But this contains 7·0 gm. of X

∴ it contains $25{\cdot}0 - 7{\cdot}0 = 18{\cdot}0$ gm. of 'sulphate' (the group SO_4).

Our problem now reduces to—*Find the simplest formula of a hydrated sulphate which contains* 7 *gm. of a metal* X (*atomic weight* 56), 18·0 *gm. of the sulphate group, and* 10·1 *gm. of water of hydration.* We write

Elements etc.	*Quantities*	*These numbers are proportional to*	*If* 1=H
X	7·0	$7 \times \frac{56}{7} = 56$	$56 = X$
'Sulphate'	18·0	$18 \times \frac{56}{7} = 144$	$144 = 1\frac{1}{2}(SO_4)$
Water	10·1	$10{\cdot}1 \times \frac{56}{7} = 80{\cdot}8$	$80{\cdot}8 = 4\frac{1}{2}H_2O$

This gives $X(SO_4)_{1\frac{1}{2}}.4\frac{1}{2}H_2O$, and the simplest formula is evidently $X_2(SO_4)_3.9H_2O$.

8. 100 *gm. of marble chips are dropped into* 500 *gm. of a solution of hydrochloric acid containing one-tenth of its weight of the pure acid. How much* (*if any*) *of the chips will remain undissolved, and what weight of anhydrous calcium chloride would be obtained on evaporating the solution?* [$Ca = 40$, $C = 12$, $O = 16$, $H = 1$, $Cl = 35{\cdot}5$.]

The equation is

$$\mathrm{Ca\;\;C\;\;O_3 + 2H\;\;\;Cl = Ca\;\;Cl_2 \qquad + H_2O + CO_2}$$
$$\underbrace{40+12+48}_{100}\quad \underbrace{2(1+35{\cdot}5)}_{73}\quad \underbrace{40+2\times 35{\cdot}5}_{111}$$

In our solution we have one-tenth of 500 gm. of pure hydrochloric acid, i.e. 50 gm.

The equation shows that

73 gm. of pure acid will dissolve 100 gm. of marble.

$\therefore$ 50 ,, ,, ,, ,, $\frac{100}{73} \times 50 = 68{\cdot}5$ gm. of marble.

But 100 gm. of marble was present.

$\therefore$ amount undissolved $= 100 - 68{\cdot}5 =$ ***31·5 gm.***

Again, the equation shows that for every 73 gm. of acid used up, 111 gm. of calcium chloride is produced.

Here, 50 gm. of acid is used up (the whole of it).

$\therefore$ wt. of calcium chloride produced $= \frac{111}{73} \times 50 =$ ***76·0 gm.***

Questions

The atomic weights required in the following calculations should be taken from the 'approximate' column in the table (end of book).

1. Calculate the percentage of

(i) Iron in ferrous sulphide, FeS.

(ii) Lead in lead sulphide, PbS.

(iii) Carbon in carbon dioxide, CO_2.

(iv) Aluminium in aluminium oxide, Al_2O_3.

2. Calculate the percentage composition of

(i) Sodium nitrate, $NaNO_3$.

(ii) Calcium carbonate, $CaCO_3$.

(iii) Silver nitrate, $AgNO_3$.

(iv) Lead sulphate, $PbSO_4$.

(v) Calcium chloride, $CaCl_2$.

(vi) Calcium hydroxide, $Ca(OH)_2$.

3. Find the percentage of water of crystallisation in each of the following:

(i) Magnesium sulphate, $MgSO_4.7H_2O$.

(ii) Copper sulphate, $CuSO_4.5H_2O$.

(iii) Calcium chloride, $CaCl_2.6H_2O$.

(iv) Sodium carbonate, $Na_2CO_3.10H_2O$.

(v) Zinc sulphate, $ZnSO_4.7H_2O$.

(vi) Calcium sulphate, $CaSO_4.2H_2O$.

4. Find the simplest formulæ for substances having the following percentage compositions:

(i) Carbon, 27·3; oxygen, 72·7.

(ii) Iron, 63·6; sulphur, 36·4.

(iii) Phosphorus, 43·7; oxygen, 56·3.

(iv) Silver, 63·5; nitrogen, 8·2; oxygen, 28·2.

(v) Potassium, 38·6; nitrogen, 13·9; oxygen, 47·5.

(vi) Copper, 25·6; sulphur, 12·8; oxygen, 25·6; water of crystallisation, 36·0.

5. Find the simplest formulæ for substances having the following percentage compositions:

(i) Carbon, 42·9; oxygen, 57·1.

(ii) Lead, 86·6; sulphur, 13·4.

(iii) Aluminium, 52·9; oxygen, 47·1.

(iv) Sodium, 43·4; carbon, 11·3; oxygen, 45·3.

(v) Hydrogen, 2·1; sulphur, 32·6; oxygen, 65·3.

(vi) Zinc, 22·7; sulphur, 11·1; oxygen, 22·2; water of crystallisation, 44·0.

6. How much mercuric oxide could be obtained from 100 gm. of mercury? (Equation on p. 46.)

7. What weight of sulphur would be required to combine with 7 gm. of iron? (Equation on p. 41.)

8. What weight of sulphuric acid would be obtained on treating 40 gm. of sulphur trioxide with water? (Equation on p. 288.)

9. Washing soda has the formula $Na_2CO_3.10H_2O$. What weight of anhydrous sodium carbonate is left when all the water of crystallisation is expelled by heating 50 gm. of washing soda? *Camb. (part)*

10. When zinc carbonate is heated, the reaction is represented by the equation $ZnCO_3 = ZnO + CO_2$. Calculate (i) the loss of weight when 2·5 gm. of zinc carbonate is heated, (ii) the weight of zinc in the residue of zinc oxide. *Camb. (part)*

11. From the equation $Zn + H_2SO_4 = ZnSO_4 + H_2$, calculate the weight of zinc sulphate obtained from 13 gm. of zinc. *O.C. (part)*

12. From the equation $CaCO_3 = CaO + CO_2$, calculate the weight of quicklime which could be obtained by heating 10 gm. of chalk. *O.C. (part)*

13. Five grams of a metal M (atomic weight 27) are converted to 61·7 gm. of a crystalline sulphate, containing 48·6% water of crystallisation. Calculate the simplest formula of the sulphate. *Camb.*

CHAPTER 6

EQUIVALENTS AND THEIR RELATION TO ATOMIC WEIGHTS

On p. 35 we saw that the ***atomic weight*** of an element is *the weight of its atom when the weight of the hydrogen atom is taken as unity* (*one*). We are not concerned with the *absolute* weight of the atom. Thus when we say that the atomic weight of carbon is 12, we simply mean that it is *twelve times as heavy as a hydrogen atom.*

It is important to know how some at least of the atomic weights given in the table at the end of the book have been obtained. We must first learn something about *equivalents* (or *equivalent weights*), and we shall find that atomic weights are closely connected with these.

We have often met with the fact that when zinc is dissolved in dilute sulphuric acid, hydrogen is *displaced* by the zinc. It is quite possible (as we shall see presently) to measure the quantities concerned, and we find that 33 gm. of zinc is required to displace 1 gm. of hydrogen. We express this by saying that—

33 gm. of zinc is ***equivalent*** to 1 gm. of hydrogen.

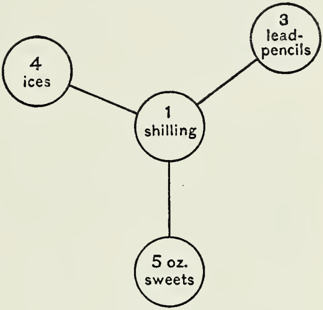

Fig. 6/1

In the same way we find 1 gm. of hydrogen is also displaced by 12 gm. of magnesium, or 28 gm. of iron, or 30 gm. of tin, and so we say that 12 gm. of magnesium is *equivalent* to 1 gm. of hydrogen (and similarly for the other metals). These numbers stand for a kind of exchange value—12 gm. of magnesium, for instance, can be exchanged for 1 gm. of hydrogen.

Now in ordinary life we are used to the idea of exchange value. Thus for one shilling we can exchange perhaps 3 lead-pencils, or 5 oz. of sweets, or 4 ices. For simplicity let us express this as shown in fig. 6/1.

Since these quantities are all related (in value) to one shilling, they are related to one another, and evidently a fair exchange for 3 lead-pencils would be either 5 oz. of sweets or 4 ices.

If now we make a similar diagram for hydrogen, etc., we get fig. 6/2*a* (never mind fig. 6/2*b* for the present).

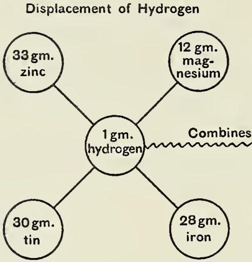

Fig. 6/2*a*

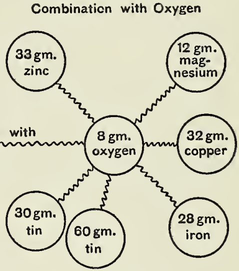

Fig. 6/2*b*

The question at once arises, 'Could 12 gm. of magnesium (for instance) be exchanged for 33 gm. of zinc, just as 3 lead-pencils can be exchanged for 4 ices?'

The obvious course is to try. When magnesium is put into zinc sulphate, the zinc is displaced—

$$Mg + ZnSO_4 = MgSO_4 + Zn$$

We can weigh the magnesium we start with, and also the zinc produced, and it turns out that 12 gm. of magnesium can indeed be exchanged for 33 gm. of zinc.

So far we have spoken only of *displacement* or exchange. We now come to the question of *combination*—8 gm. of oxygen, for instance, will combine with 1 gm. of hydrogen. By careful experiment it is found that 8 gm. of oxygen will also combine with 12 gm. of magnesium, or with 33 gm. of zinc, etc. (see fig. 6/2*b*). You will remember that these numbers (12, 33, etc.) were obtained as being the number of grams of the particular metal which would displace 1 gm. of hydrogen. We see now that they *could* have been obtained in another way—by finding how many grams of the particular metal would combine with 8 gm. of oxygen. This alternative method is sometimes very useful. Copper, for instance, will not displace hydrogen—nothing happens when we pour dilute hydrochloric or sulphuric acid on this metal—and so we cannot find how many grams of copper displace 1 gm. of hydrogen. But copper combines readily enough with oxygen, and it is quite easy to find that 32 gm. of copper are required to combine with 8 gm. of oxygen. We therefore conclude that if copper *did* displace hydrogen, 32 gm. of it would be required to displace 1 gm.

We are now in a position to understand the following definition: *The* ***equivalent*** *(or* ***equivalent weight****) of an element is the number of grams of that element which will combine with, or displace, either one gram of hydrogen or eight grams of oxygen.*

Note that the equivalent of an element is a *number*, not a weight. For instance, the equivalent of oxygen is 8, not 8 gm. If we wish to indicate a weight we use the term 'gram-equivalent'—the gram-equivalent of oxygen is 8 gm.

The Law of Equivalents. We have already seen that 33 gm. of zinc can be replaced by 12 gm. of magnesium, 33 and 12 being the respective equivalent weights of these metals.

Again, 23 gm. of sodium will replace 1 gm. of hydrogen, and 35·5 gm. of chlorine will combine with 1 gm. of hydrogen, so that the equivalents of sodium and chlorine are 23 and 35·5 respectively. Now we find that sodium and chlorine combine with one another in the proportions of 23 and 35·5. These facts and thousands of others are summed up in the following statement known as the ***Law of Equivalents*** or ***Law of Reciprocal Proportions***. *The quantities of elements which combine with or displace one another are in proportion to their equivalent weights, or to some simple multiple of those weights.*

The examples we mentioned (zinc and magnesium, sodium and chlorine) would have been covered without the last eight words of the statement, but cases often arise (as in the following example) in which this extra clause is needed.

Illustrate the Law of Equivalents by means of the following facts:

(a) *Nitrous oxide contains* 36·3 *per cent. of oxygen by weight.*

(b) *Water contains* 88·8 *per cent. of oxygen by weight.*

(c) *Ammonia contains* 82·2 *per cent. of nitrogen by weight.*

(*b*) and (*c*) evidently give us the means of calculating the equivalents of oxygen and nitrogen respectively. Let us obtain these, and then find how our results compare with the information given in (*a*).

From (*b*), 88·8 gm. of oxygen combines with 11·2 gm. hydrogen.

$$\therefore \text{ equivalent of oxygen} = \frac{88{\cdot}8}{11{\cdot}2} = 7{\cdot}93.$$

From (*c*) 82·2 gm. of nitrogen combines with 17·8 gm. of hydrogen.

$$\therefore \text{ equivalent of nitrogen} = \frac{82{\cdot}2}{17{\cdot}8} = 4{\cdot}62.$$

From (*a*) we see that 36·3 gm. of oxygen combines with 63·7 gm. of nitrogen.

$\therefore$ 7·93 gm. of oxygen (i.e. the gm.-equivalent) combines with $\frac{63{\cdot}7}{36{\cdot}3} \times 7{\cdot}93 = 13{\cdot}9$ gm. of nitrogen.

Now 13·9 is almost exactly three times 4·62, i.e. three times the equivalent of nitrogen.

Thus the equivalent of oxygen combines with a *simple multiple* of the equivalent of nitrogen.

Boyle's and Charles' Laws. We shall presently consider the methods by which equivalents are obtained. Before doing so, however, we must spend a little time over Boyle's and Charles' Laws, because unless we can apply these we shall often find ourselves unable to work out the results we have obtained.

As you have probably studied these laws in your Physics lessons, we shall content ourselves here with stating them, and working out a few examples based on them.

Boyle's Law. *If the temperature of a given mass of gas remains constant, its volume will vary inversely as the pressure.*

Charles' Law. *If the pressure of a given mass of gas remains constant, its volume will be proportional to its absolute temperature.*

N.B. (i) Pressure is measured in terms of a column of mercury. E.g. when we say that the pressure of the air is 74 cm., we mean that it will support a column of mercury 74 cm. in height.

(ii) 'Absolute temperature' is obtained by adding 273 to the Centigrade temperature. E.g. 100° C = 373° Abs.

(iii) A temperature of 0° C. is said to be 'normal' or 'standard,' and so is a pressure of 76 cm. 'N.T.P.' or 'S.T.P.' ('normal' or 'standard' temperature and pressure) means a temp. of 0° C. and a pressure of 76 cm.

(iv) Both laws are included in the 'General Gas Law,' expressed by the equation $P_1V_1/T_1 = P_2V_2/T_2$. For if $T_1 = T_2$, we have $P_1V_1 = P_2V_2$, or $V_1/V_2 = P_2/P_1$ (Boyle's Law); while if $P_1 = P_2$, we have $V_1/T_1 = V_2/T_2$, or $V_1/V_2 = T_1/T_2$ (Charles' Law).

Example 1. *A boy collected 380 c.c. of hydrogen at a pressure of 74 cm. What volume would he have obtained if the pressure had been 76 cm., the temperature remaining constant?*

Begin by putting down the given volume, 380 c.c. Your knowledge of 'proportion' in arithmetic tells you that you must multiply *either* by $\frac{74}{76}$ *or* by $\frac{76}{74}$. Which?

If the pressure had been 76 instead of 74, i.e. *greater*, the volume would have been *less*.

∴ we multiply by $\frac{74}{76}$, and so volume $= 380 \times \frac{74}{76} = \boldsymbol{370}$ **c.c.**

Example 2. *The hydrogen collected above was measured at 12° C. What would have been its volume at 0° C., the pressure remaining constant?*

$$12° \text{ C.} = 273 + 12 = 285° \text{ Abs.}$$
$$0° \text{ C.} = 273 + 0 = 273° \text{ Abs.}$$

Our sum is now a straightforward exercise in proportion. 'If 380 c.c. is the volume at a temperature of 285° Abs., what is the volume at 273° Abs?'

Clearly the volume will be *less* at the lower temperature. We therefore multiply the given volume by $\frac{273}{285}$.

I.e. required volume $= 380 \times \frac{273}{285} = \boldsymbol{364}$ **c.c.**

***Example 3.** If 380 c.c. is the volume of a quantity of hydrogen when the temperature is 12° C. and the pressure is 74 cm., what would be the volume at N.T.P.?*

This can be worked 'from first principles' (as in the two preceding examples), but here it is perhaps simpler to use the equation $P_1V_1/T_1=P_2V_2/T_2$.

We have $P_1=74$ cm., $V_1=380$ c.c., $T_1=12+273=285°$ Abs.
$P_2=76$ cm., $V_2=$? $T_2=273°$ Abs.

∴ substituting in the equation we have

$$\frac{74\times 380}{285}=\frac{76\times V_2}{273}, \text{ giving } V_2=\frac{380\times 74\times 273}{76\times 285}=\mathbf{354{\cdot}4\ c.c.}$$

N.B. (i) In all temperature and pressure calculations it is a good plan before 'multiplying out' to make sure that the standard numbers 273 and 76 are on opposite sides, i.e. if 273 is in the numerator, 76 must be in the denominator and *vice versa*. If this is not the case there is something wrong.

(ii) Instead of 'c.c.' the student must be prepared to meet with 'ml.'(=millilitre). An example occurs in Question 4 on p. 69.

Determination of Equivalents. We are now ready to consider some of the methods by which the equivalents of elements are found. These will be dealt with under the following heads:

(i) Displacement of hydrogen.
(ii) Combination with oxygen.
(iii) Displacement of one metal by another.
(iv) The method of electrolysis.

We shall also discuss a method for determining the equivalent of oxygen. Except for this, the methods described will be such as apply only to metals. The methods required in the case of non-metals call for much more elaborate apparatus and a much higher degree of practical skill.

Method (i). Displacement of Hydrogen. A suitable metal for this experiment is zinc. The apparatus of fig. 6/3 is very often employed, where B is a 'Winchester quart' and A a small conical flask containing dilute sulphuric or hydrochloric acid.

A weighed quantity of metal is placed in the little tube F, supported inside the flask by a thread in the way shown. When all is ready, the cork of A is loosened for a moment, and tightened again as soon as the tube has fallen. The acid is now in contact with the metal. Hydrogen is given off, and when this passes into the Winchester quart it drives an equal volume of water into the receiver D.

When the metal has completely dissolved, it will be found that the flask A is warm as the result of the chemical action. It should be allowed to cool down while E remains under the water which has been collected. As A cools down, a little water will be drawn back. The volume that remains will correspond to the volume of 'cooled down' hydrogen, the temperature of which may be taken as the temperature of the water in the big bottle.

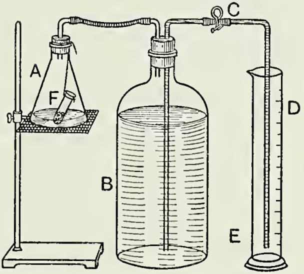

FIG. 6/3. Equivalent of zinc, etc.

Before measuring the water in the receiver, however, raise the latter until the surface of the water in it is level with that in the Winchester quart. The *pressure* of the hydrogen is now that of the atmosphere,[1] and can be obtained by reading the barometer. Fix the clip while the receiver is in the raised position, and, by means of a graduated cylinder, measure the water it contains. Suppose the following results have been obtained:

Wt. of zinc	2·20 gm.
Vol. of water (=vol. of hydrogen)	800 c.c.
Temperature	14° C.
Pressure	74·6 cm.

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[1] It is really *less* than this by the pressure of the enclosed water vapour. E.g. suppose temperature of water in large bottle is 14° C.

Maximum pressure of water vapour at 14° C.=1·2 cm.

∴ true pressure of hydrogen=74·6 − 1·2=73·4 cm.

When in a given calculation the vapour pressure is stated, it must be taken into account. Otherwise (as above) it may be ignored.

We must find the volume of the hydrogen at N.T.P. (cf. Example 3 above).

$$\text{Vol. at N.T.P.} = 800 \times \frac{74{\cdot}6}{76} \times \frac{273}{287} = 747 \text{ c.c.}$$

It is usual to assume in these calculations that 1 litre of hydrogen at N.T.P. weighs 0·09 gm.

$$\therefore \text{ wt. of 747 c.c. of hydrogen} = \frac{0{\cdot}09}{1000} \times 747 = 0{\cdot}0672 \text{ gm.}$$

∴ 0·0672 gm. hydrogen has been displaced by 2·20 gm. zinc.

$$\therefore \text{ 1 gm. hydrogen is displaced by } \frac{2{\cdot}20}{0{\cdot}0672} = 32{\cdot}7 \text{ gm. zinc.}$$

∴ *32·7* is the *equivalent* of zinc (since 32·7 gm. of zinc displaces 1 gm. of hydrogen).

If we had taken vapour pressure into account (footnote, p. 61), we should have had—

True pressure of hydrogen = 74·6 – 1·2 = 73·4 cm.

$$\therefore \text{ Vol. at N.T.P.} = 800 \times \frac{73{\cdot}4}{76} \times \frac{273}{287} = 735 \text{ c.c.}$$

$$\text{Wt. of this hydrogen} = \frac{0{\cdot}09}{1000} \times 735 = 0{\cdot}0661 \text{ gm.}$$

$$\therefore \text{ Equivalent} = \frac{2{\cdot}20}{0{\cdot}0661} = \mathbf{33{\cdot}3}.$$

The difference between the two answers (32·7 and 33·3)—nearly 2%—is quite appreciable.

Method (*ii*). *Combination with Oxygen.* A weighed quantity of the metal is completely oxidised, and the oxide is weighed. If x = wt. of metal and y = wt. of oxide, then $y - x$ = wt. of oxygen.

$y - x$ gm. of oxygen combines with x gm. of metal.

∴ 1 ,, ,, ,, $\frac{x}{y-x}$ gm. of metal.

∴ 8 ,, ,, ,, $\frac{x}{y-x} \times 8$ gm. of metal.

$$\text{I.e. equivalent} = \frac{8x}{y-x}.$$

The best way to oxidise the metal is to dissolve it in nitric acid, thus forming the nitrate. The nitrate is evaporated to dryness and strongly heated, whereby it is decomposed into the oxide (nitrogen dioxide and oxygen being given off, p. 340).

The experiment is conveniently carried out by weighing a dry test-tube, introducing about a gram of the metal (copper, for instance) and then weighing again. Concentrated nitric acid[1] is then added, a few drops at a time—if much is added the action becomes too violent and some of the solution froths out of the test-tube. When the metal has completely dissolved, the solution is evaporated to dryness (without removing it from the test-tube). The residue is then heated strongly until brown fumes cease to be evolved, and it is afterwards cooled and weighed. To make sure that decomposition (of nitrate) is complete, the test-tube should be heated for two or three minutes longer, and again weighed. There should be no further change of weight.

Example

Wt. of test-tube	17·48 gm.
Test-tube + copper	18·53 ,,
Final wt. of test-tube + copper oxide	18·79 ,,
Wt. of copper = 18·53 – 17·48	= 1·05 ,,
Wt. of oxygen = 18·79 – 18·53	= 0·26 ,,

To combine with 0·26 gm. of oxygen we require 1·05 gm. of copper.

$\therefore$ to combine with 8 gm. of oxygen we require $\frac{1\cdot05}{0\cdot26} \times 8$ gm.
= 32·3 gm. of copper.

I.e. equivalent = ***32·3***.

We may vary the above method by *starting* with the oxide[2] and reducing it to the metal by means of a stream of hydrogen or (more conveniently) coal-gas, the experiment being carried out as already described on p. 25.

Example

Wt. of porcelain boat	5·82 gm.
Boat + copper oxide	7·82 ,,
Boat + copper (after expt.)	7·42 ,,
$\therefore$ wt. of oxygen = 7·82 – 7·42	= 0·40 ,,
wt. of copper = 7·42 – 5·82	= 1·60 ,,

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[1] The action is steadier if the ordinary bench acid (sp. gr. 1·42) is first diluted with about one-third its volume of water.

[2] A very easy exercise consists in obtaining the equivalent of mercury. The method is perhaps sufficiently indicated by Question 9, p. 69.

To combine with 0·40 gm. of oxygen we require 1·60 gm. of copper.

∴ to combine with 8 gm. of oxygen we require $\frac{1\cdot60}{0\cdot40} \times 8$ gm.
=32·0 gm. of copper.

I.e. equivalent=***32·0.***

Method (*iii*). *Displacement of One Metal by Another.* If iron is placed in a solution of copper sulphate, the copper is displaced according to the following equation:—

$$Fe + CuSO_4 = FeSO_4 + Cu$$

If we weigh the iron, and afterwards wash, dry and weigh the copper, we can find the equivalent of one of the metals providing we know that of the other. Suppose, for instance, the equivalent of iron has been found by Method (i) to be 28·0, and that, starting with 2·00 gm. of iron, we were able to displace 2·27 gm. of copper. Then—

2 gm. of iron displaces 2·27 gm. of copper.

∴ 28 gm. of iron displaces $\frac{2\cdot27}{2} \times 28 = 31\cdot78$ gm. of copper.

But 28 gm. of iron is equivalent to 1 gm. of hydrogen.

∴ 31·78 gm. of copper is equivalent to 1 gm. of hydrogen.

I.e. equivalent of copper=***31·78.***

This method may be used for many pairs of metals. In the experiment just described we might, for instance, have used zinc or magnesium instead of iron. In fact, we may say generally that if we have two metals, A and B, *either* A will displace B from a solution of a salt of B, *or* B will displace A from a solution of a salt of A.

Method (*iv*). *Electrolysis.* This will be discussed in Chapter 34.

Equivalent of Oxygen. In several of the preceding examples we have assumed this to be 8. The number may be determined by the experiment already described on p. 26. There we found that 5·3 6gm. of oxygen combined with 0·67 gm. of hydrogen. Clearly the amount combining with *one* gram of hydrogen is 5·36 ÷ 0·67 = 8·00 gm., and so the equivalent of oxygen is 8·00.

Equivalents and Atomic Weights. As we mentioned at the beginning of this chapter, equivalents are important because they are closely related to the subject of atomic weights. Let us try to understand the connection between these two quantities.

The weight of oxygen in water is eight times that of the hydrogen. This is true for the smallest quantities of water we are able to examine, and if we accept the Atomic Theory we must believe that it is true for the smallest quantity of water that can possibly exist, namely, for the molecule.

Now, *if* the molecule of water consists of one atom of oxygen combined with one atom of hydrogen—i.e. if the formula for water is HO—the atomic weight of oxygen must be 8. (For there is one atom of hydrogen present, weighing one unit, and the weight of the oxygen present has been found to be eight times this.)

If, however, the molecule of water contains *two* atoms of hydrogen and one of oxygen—i.e. if its formula is H_2O—then the oxygen atom must weigh eight times as much as *two* hydrogen atoms, which would be 16 units. Similarly, if the formula were H_3O, the atomic weight of oxygen would be 24.

It is important to note also that if the formula of water is HO, the *valency* of oxygen (i.e. the number of atoms of hydrogen with which one atom of oxygen combines) is 1. If the formula is H_2O, the valency of oxygen is 2, and so on. Summarising the situation, we have—

By Experiment. 8 gm. of oxygen combine with 1 gm. of hydrogen, i.e. equivalent of oxygen = 8.

If formula is	*Valency is*	*Atomic weight as explained above is*	*Equivalent* (8) × *valency*
HO	1	8	$8 \times 1 = 8$
H_2O	2	16	$8 \times 2 = 16$
H_3O	3	24	$8 \times 3 = 24$

With a little thought we begin to see that the 'atomic weight as explained above' was really arrived at by multiplying the equivalent weight by the valency, and this is true, not simply for the particular substance we have taken, but for other substances as well. In short—

$$\text{(atomic weight)} = \text{(equivalent)} \times \text{(valency)}$$
$$\text{or } A = EV.$$

The valency V is a small whole number which very rarely exceeds 5. It will be clear, then, that when we have found the *equivalent* of an element, we have only to multiply this equivalent by some small whole number to obtain the atomic weight. But how are we to find this 'small whole number'?

Dulong and Petit's Law. Dulong and Petit in 1819 discovered a simple law which helps us, in many cases, to answer the question just stated. They noticed that elements with high atomic weights had low specific heats, and *vice versa*. Naturally they wondered whether this was a case of 'inverse proportion,' i.e. whether the atomic weight was high in *proportion* as the specific heat was low (just as in Boyle's Law the volume is high in proportion as the pressure is low).

Now the easy test for inverse proportion is to multiply together the two quantities concerned and see whether the product is constant (e.g. in Boyle's Law a constant number is obtained when we multiply pressure by volume). On multiplying the various atomic weights by the corresponding specific heats, they found that the product was *roughly* constant, coming to about 6·3. This constant they called the ***Atomic Heat***. Some examples are given in the following table, but as atomic weights were not known with much accuracy in 1819 we have given the modern numbers. We have also included one or two elements which were scarcely known to Dulong and Petit.

Element	*Atomic weight* (A)	*Specific heat* (H)	*Atomic heat* (=A × H)
Aluminium	27	0·217	5·9
Copper	64	0·093	6·0
Iron	56	0·113	6·3
Lead	207	0·031	6·4
Magnesium	24	0·248	6·0
Silver	108	0·056	6·0
Sodium	23	0·300	6·9
Sulphur	32	0·173	5·5
Tin	119	0·054	6·4
Zinc	65	0·092	6·0

Dulong and Petit's Law may be stated thus: *When the atomic weight of a solid element is multiplied by its specific heat, the product obtained is roughly constant and equal to about* 6·3.

If the product had been *exactly* constant we could easily have obtained the atomic weight of any solid element. We should simply have found its specific heat and divided this into 6·3. Even as it is, the law is very useful in helping us to arrive at exact atomic weights. This will be best seen from an example.

The equivalent of an element has been found to be 8·99, *and its specific heat* 0·217. *Find its atomic weight.*

We have seen that $A=EV$, where V is the valency (a small whole number).

Now $E=8\cdot99$.

$\therefore$ A is *one* of the numbers 8·99, 17·98, 26·97, 35·96 . . . according as V is 1, 2, 3, 4. . . .

To get a *rough* value of the atomic weight we divide 6·3 by 0·217, getting 29. Of the possible values mentioned above, we therefore select ***26·97*** because this is the one lying nearest to 29.

Here is another example.

2 *gm. of a certain metal M, on treatment with nitric acid and subsequent ignition, yielded* 2·504 *gm. of oxide. The specific heat of the metal was found to be* 0·093. *Find its equivalent, its atomic weight, and its valency. Also write down the formulæ of its oxide and chloride.*

0·504 gm. of oxygen combines with 2 gm. of M.

$\therefore$ 8 ,, ,, ,, $\frac{2}{0\cdot504}\times 8=31\cdot76$ gm. of M.

31·76 is therefore the equivalent (by definition).

From $A=EV$, we know that the atomic weight is *one* of the numbers 31·76, 63·52, 95·28 . . . according as $V=1, 2, 3$ . . .

But specific heat $=0\cdot093$.

$\therefore$ atomic weight is *roughly* $6\cdot3\div0\cdot093=68$.

Of the possible values we therefore choose ***63·52***, and evidently ***$V=2$***.

As the metal is divalent, its oxide will have the formula ***MO*** and its chloride ***MCl_2***.

More than One Equivalent. Let us go back to the relation $A=EV$, or $E=A\div V$. For any one element, the atomic weight A is constant (by the atomic theory). If there is more than one value of V, there will correspondingly be more than one value of E.

Copper, for instance, forms two oxides, cuprous oxide Cu_2O and cupric oxide CuO. In the first the valency is 1, in the second 2. The atomic weight of copper is 63·6. Thus the equivalent of copper in the first oxide is 63·6 ÷ 1 = 63·6, while its equivalent in the second is 63·6 ÷ 2 = 31·8. Note the simple numerical relationship between the two values (63·6 : 31·8 = 2 : 1). This follows, of course, from the fact that the valencies are small whole numbers..

It also follows from the Law of Multiple Proportions. In the two oxides let us consider a fixed weight of oxygen, 8 gm. Let c_1 be the weight of copper combined with this 8 gm. of oxygen in cuprous oxide, and let c_2 be the corresponding quantity in cupric oxide. c_1 and c_2 are by definition the equivalents. But by the Law of Multiple Proportions c_1 and c_2 are in a simple ratio; therefore the *equivalents* are in a simple ratio.

Conversely, when equivalents have been found to be in a simple ratio, we are supplied with an example of the law of Multiple Proportions. For in the case of equivalents, 'the weight of one of the elements *is* the same in each' (e.g. 8 gm. of oxygen), and so, if the equivalents are in a simple ratio, it is 'the weights of the other element' that are in a simple ratio, thus illustrating the law.

Questions

N.B. *In all the following calculations, unless alternative information is given in the question, it is to be assumed that* (i) *atomic weights are as given in the 'approximate' column in the table* (*end of book*), *and* (ii) 1 *litre of hydrogen at N.T.P. weighs* 0·09 *gm.*

1. What volume would be occupied at N.T.P., by a quantity of gas which occupies—

(i) 288 c.c. at 15° C. and 74 cm.?
(ii) 304 c.c. at −48° C. and 75 cm.?
(iii) 570 c.c. at 12° C. and 72 cm.?

2. 32 gm. of oxygen occupies 22·4 litres at N.T.P. What volume would this mass of gas occupy at—

(i) 12° C. and 57 cm.?
(ii) −25° C. and 62 cm.?
(iii) 15° C. and 56 cm.?

3. (*a*) To what temperature would 60 c.c. of air at 17° C. and 740 mm. pressure have to be raised so that, without change of pressure, its volume would be doubled?

(*b*) What pressure would now have to be applied so that, at the new temperature, the volume would be brought back to 60 c.c.?

4. A certain mass of gas occupies 250 ml. at 87° C. and 72 cm. pressure. What pressure would be required so that the gas should occupy 100 ml. at 15° C.?

5. The air inside a sealed flask is at a pressure of 78 cm. and the temperature 15° C. If the temperature is raised to 159° C. what will the pressure become?

6. 'Hydrolith' (calcium hydride) contains 95·24 per cent. of calcium, and calcium oxide contains 71·43 per cent. Water contains 88·89 per cent. of oxygen. Show that from these facts we may obtain an illustration of the Law of Equivalents.

7. Carbon dioxide contains 27·27 per cent. of carbon and 72·73 per cent. of oxygen. Marsh gas (CH_4) contains 75 per cent. of carbon and 25 per cent. of hydrogen. Water contains 11·11 per cent. of hydrogen and 88·89 per cent. of oxygen. State the important law which is indicated by these figures, and show from them that the law is satisfied. *W.J.*

8. Find the equivalents of zinc, aluminium and magnesium respectively from the following data: (i) 2·3 gm. of zinc displaced 0·0704 gm. of hydrogen from sulphuric acid; (ii) 1·8 gm. of aluminium displaced 0·2 gm. of hydrogen from hydrochloric acid; (iii) 0·12 gm. of magnesium displaced 0·01 gm. of hydrogen from sulphuric acid.

9. On heating 5·4 gm. of mercuric oxide it decomposed leaving 5·0 gm. of mercury. Find the equivalent of mercury.

10. Oxides of copper, lead and iron were reduced by coal gas with the following results: (i) 4 gm. of copper oxide yielded 3·2 gm. of copper; (ii) 5·57 gm. of lead oxide (litharge) yielded 5·17 gm. of lead; (iii) 4 gm. of ferric oxide yielded 2·8 gm. of iron. Calculate the equivalents of copper, lead and iron.

11. Magnesium, copper and zinc were converted into their oxides by first dissolving them in nitric acid and then heating the nitrates (p. 63). Using 3 gm. of the metal in each case, it was found that the magnesium gave 4·97 gm. of oxide, copper gave 3·76 gm. and zinc 3·73 gm. Calculate the equivalent of each metal.

12. In finding the equivalent of zinc by the method described on p. 61 three boys obtained the following results:

	1st Boy	*2nd Boy*	*3rd Boy*
Wt. of zinc	1·5 gm.	2 gm.	2·5 gm.
Vol. of hydrogen	555 c.c.	750 c.c.	910 c.c.
Temperature	15° C.	16° C.	17° C.
Barometer reading	75 cm.	75 cm.	75 cm.

Find in each case: (i) the volume corrected to N.T.P.; (ii) the weight of the hydrogen (3 significant figures); (iii) the equivalent.

13. Recalculate the above, taking into account the vapour pressure of water. (This is 1·3 cm. at 15° C., 1·4 cm. at 16° C. and 1·4 cm. at 17° C., correct to one decimal place.)

14. 2·4 gm. of iron displaced 2·72 gm. of copper from a solution of copper sulphate. If the equivalent of iron is 28·0 find that of copper.

15. 0·30 gm. of magnesium displaced 2·65 gm. of silver from a solution of silver nitrate. If the equivalent of magnesium is 12·2, find that of silver.

16. Dry hydrogen was passed over 3·18 gm. of black copper oxide heated in a hard glass tube. When the reduction was complete, 2·54 gm. of copper was left and 0·72 gm. of water was collected. Calculate (*a*) the composition of water by weight, (*b*) the equivalent of copper.

Draw a labelled diagram of the apparatus necessary to perform this experiment. (A description of the experiment is not required.) Give the names of two scientists associated with the investigation of the composition of water. *Brist.*

17. Define (*a*) valency, (*b*) equivalent.

A certain metal M has a valency of 3 and its atomic weight is 54·9. Write down: (i) the formula of the chloride of the metal M, (ii) the formula of the sulphate of the metal M, (iii) the equivalent of the metal M. What weight of the metal M would replace 2 gm. of hydrogen? *W.J.*

18. State, without description, *four* methods by which the equivalent weight of a metal may be determined.

Which method would you use, and why, to find the equivalent weight of (*a*) magnesium, (*b*) copper, (*c*) lead? Describe *one* of these methods in essential detail. *Oxf.*

19. The specific heat of a certain metal is 0·11, and its equivalent is 18·6. What multiple of the equivalent weight is the atomic weight? *Oxf.* (*part*)

20. Define the Equivalent Weight of an element. How is the Equivalent Weight related to the Atomic Weight?

An element M has an atomic weight of 27 and an equivalent weight of 9. Write down the formulæ for its oxide and its sulphate. *Lond.* (*part*)

21. Define the terms (*a*) equivalent weight of an element, (*b*) atomic weight, (*c*) valency.

When 3·014 gm. of a metallic oxide was reduced it yielded 2·374 gm. of the metal. If the specific heat of the metal was 0·056, calculate (i) the equivalent weight, (ii) the valency, (iii) the accurate atomic weight of the metal. *Camb.*

22. What do you understand by the terms *element, atom, compound*?

(*a*) A metal of specific heat 0·11 forms an oxide which contains 30% oxygen. Calculate (i) the equivalent of the metal, (ii) its approximate atomic weight, (iii) its accurate atomic weight.

(*b*) A metal M, of atomic weight 52, forms an oxide which contains 31·6% oxygen. Calculate the simplest formula of the oxide. (O=16.) *Camb.*

23. What is meant by the terms 'atom', 'valency' and 'atomic weight'?

The specific heat of a metal is 0·093. If 3·25 gm. of the metal forms 4·05 gm. of oxide on oxidation, what is the exact atomic weight of the metal?

Show clearly the steps involved in your calculation. *Dur.*

24. Describe how you would measure the volume of hydrogen evolved when a small amount of zinc is dissolved in sulphuric acid. In an experiment, 0·297 gm. of a certain bivalent metal, 'M', when dissolved in an acid, set free 179 c.c. of dry hydrogen. The gas was measured at 18° C. and 738 mm. What is the atomic weight of the metal 'M'?

Write down the formula of (*a*) the hydroxide, and (*b*) the carbonate of the metal 'M'.

1000 c.c. of hydrogen at N.T.P. weighs 0·09 gm. *Dur.*

25. M is the symbol of a trivalent metal. Write down the formula of: (i) its oxide; (ii) its hydroxide; (iii) its sulphate. If the atomic weight of M is 27, what is its equivalent weight? *W.J.* (*part*)

26. 1·2 gm. of a certain metal when *burnt* in oxygen yield 2 gm. of *oxide*. 6·0 gm. of the same metal, heated in steam, yield 10·0 gm. of oxide. Calculate the *equivalent* of the metal in each case. Write down the law of chemistry thus illustrated and explain the meaning of the words in italics. *Oxf.*

27. Two oxides of a metal contain respectively 7·175 and 13·39 per cent. of oxygen. Calculate the two equivalent weights of the metal and state clearly the law they illustrate.

If its specific heat is 0·031, find its exact atomic weight, and write down its two valencies and the formulæ of its two oxides. *Oxf.*

28. A metal has a specific heat of 0·056 and forms a chloride which contains 54·4 per cent. of chlorine. Find (i) the equivalent weight and (ii) the atomic weight of the metal: Taking M as the symbol of the metal, write the formula of its chloride. (Cl=35·5.)

29. Calculate the equivalent weights of a metal, A, from each of the following: (i) an oxide of A contained 70% of A;

(ii) 1 gm. of A displaced 1·14 gm. of copper from copper sulphate.

Show that these two equivalents illustrate the law of multiple proportions. (Cu=64.) *O.C.* (*part*)

CHAPTER 7

OLD IDEAS ABOUT THE AIR AND COMBUSTION

You have no doubt seen and done a number of experiments on the composition of air and the subject of combustion. We must now go into these questions more thoroughly, but before doing so we will step back some 250 or 300 years—to the Stuart period—and consider the views that were held then. Only very slowly did men gain the idea that during burning and rusting a substance is really combining with one special constituent of the air.

In the seventeenth century we find a number of thinkers and experimenters who put forward some very shrewd suggestions. There was the French doctor Jean Rey for instance. A friend of his had heated 2 lb. 6 oz. of tin for six hours in an open furnace. He obtained a white powder (which we should now call tin oxide), and was so excited when he found that the powder was 7 oz. heavier that he wrote to Rey for an explanation. He had also noticed that lead showed an increase in weight when heated.

Now Rey had carried out some experiments on air, and he knew that air possessed *weight.* He came to the conclusion that, during the process of heating, the air acquires a sort of stickiness, and particles of it then cling to the metal, making it heavier. He had no idea that the air consisted of two parts, and that only one of these was acting upon the metal. His conclusions were published in 1630.

In 1665 a great advance was made by Robert Hooke, who at one time had acted as assistant to Boyle[1] (discoverer of the famous Boyle's Law). Hooke had found that if a piece of charcoal or sulphur is thrown into molten nitre (saltpetre) it burns very brightly. Evidently there was something in the nitre which helped the charcoal to burn, and he concluded that air contains a substance that is 'like, if not the very same with, that which is fixed in saltpetre.' We know now that he was right—for oxygen is 'fixed in saltpetre.'

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[1] Boyle himself experimented on the subject, and confirmed the fact that tin increases in weight when heated for a long time in air. He concluded, however, that the tin had combined with particles of *fire* ('igneous corpuscles').

John Mayow (in 1674) went further still. He carried out experiments similar to Hooke's, and other experiments as well. As a result he came to the definite conclusion that air consists of two gases, one of which will allow combustion and respiration to go on, and another which will allow neither.

Looking back over the years 1630 to 1674, we see that men were rapidly getting nearer to a true answer to the question, 'What really happens when a substance burns?' Now came a serious setback.

In 1669 a German chemist named Becher had written a book in which he explained that all combustible bodies contain a peculiar kind of earth which he called 'terra pinguis.' When the body burns, this rushes out. Burning, in fact, is simply loss of terra pinguis.

Very likely nobody would have taken much notice of these ideas but for one circumstance. It happened that Becher had a very brilliant pupil named Stahl, who became so famous that everything he taught was listened to with great attention. In 1702 Stahl arranged for his old master's book to be republished, together with a long introduction by himself. 'Terra pinguis' was re-christened 'phlogiston' from a Greek word meaning flame, and so the Becher–Stahl theory is now always called the Phlogistic theory. Let us see how the phlogistonists answer certain questions.

Qu. 1. Why will a substance not burn unless air is present?

Ans. Because, in order to burn, the substance must get rid of its phlogiston, and therefore something must be present to absorb this phlogiston. That something is the air.

Qu. 2. Why does a candle soon go out if placed in a closed jar of air?

Ans. Because the air has absorbed so much phlogiston that it is saturated with it and can absorb no more—just as a soaked sponge can absorb no more water.

Qu. 3. Does charcoal contain phlogiston?

Ans. Yes. Pure charcoal burns completely away, so probably it contains a great deal of phlogiston. Possibly indeed it *is* phlogiston.

Qu. 4. What happens if you restore phlogiston to the burnt ashes of a substance?

Ans. The original substance is restored. Thus when zinc shavings are burnt, a white 'calx' is obtained. On heating this calx with charcoal, which is rich in phlogiston, zinc is once more obtained.

Qu. 5. Rey, Boyle and others all report that the calx of a metal is heavier than the metal itself. If the metal *loses* phlogiston when heated, ought not the calx to weigh less?

Ans. This question is certainly difficult. But suppose a man were holding on to a captive balloon. His weight would seem to be small while he held on, but would increase if he let the balloon escape. Even so, a metal increases in weight when its phlogiston escapes. Phlogiston is the principle of levity.

On the whole, the phlogistonists were able to make out a very good case, and their theory held the field till about the year 1780. Some men, however, were very suspicious about the 'principle of levity'; they did not see how a substance could weigh less than nothing. Chief among the doubters was the great French chemist Lavoisier, who in 1772 began a series of experiments which in the long run upset the theory altogether.

Lavoisier carried out again some of the old experiments on the heating of metals, and devised new ones. He showed that when a metal is heated in air, not only does it gain in weight, but the air loses an equal amount. He felt sure that something from the air went *into* the metal (the phlogistonists of course said that something—phlogiston—went *from* the metal into the air). His trouble was that he could never produce this 'something.' With our present knowledge, we can understand his difficulty. It is easy enough, for instance, to make copper take up oxygen on heating, forming black copper oxide; but we cannot easily make copper oxide give up its oxygen.

In October 1774, however, the English chemist Priestley visited Paris and dined with Lavoisier. He told him that a few weeks previously, by heating *mercurius calcinatus per se* (mercuric oxide as we should now call it), he had obtained a gas which made a glowing splint burst into flame. Lavoisier was all attention. Here was the 'something' for which he had been hunting so long!

He now carried out the experiment illustrated in fig. 7/1. He placed a quantity of mercury, M, in what he called a 'matrass'—really a flask with the neck drawn out and turned up at the end. This turned-up end entered a jar of air which was enclosed over more mercury. He now heated the mercury, M, for day after day by means of a furnace keeping it just below its boiling-point. The volume of air in the jar became less and less, and after about a week it had been reduced from 50 to 42 cub. in. After this there was no further change, and at the end of twelve days Lavoisier extinguished the fire.

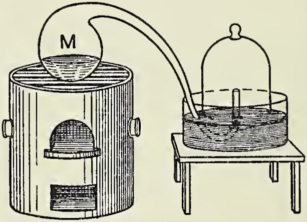

FIG. 7/1. Lavoisier's experiment

He now collected the red powder which had settled on the surface of the mercury and heated it. The gas which came from it measured 8 cub. in.! Mercury remained on the sides of the vessel in which he had heated the powder.

His experiment showed clearly that the red powder was not mercury *minus* something (phlogiston), but mercury *plus* something, and that the 'something,' together with mercury, could be obtained on heating the powder. His experiment, and more especially his careful reasoning about it, dealt the death-blow to the phlogiston theory.

After 1779, when Lavoisier published an account of his experiments, the phlogistic theory rapidly lost ground. Many chemists, however, who had grown up with the old ideas, found it difficult to accept the new point of view, and so the phlogistic theory lingered on for another twenty or thirty years. Priestley himself, for instance, remained a phlogistonist to the end of his life (he died in 1804), although his discovery of oxygen was the very thing which had enabled Lavoisier to prove that the old theory was false.

The discovery of the true nature of combustion may be said to mark the beginning of modern chemistry, so it is no wonder that Lavoisier is considered to be among the very first of the world's great scientists. 'La République n'a pas besoin de savants,' said the president of the tribunal which condemned him. It is a thousand pities that such a great man could not have been allowed to continue his work.

Questions

1. When tin is heated in the air it oxidises according to the equation $Sn + O_2 = SnO_2$. What would have been the correct increase in weight in the experiment by Jean Rey's friend (p. 73)? Can you suggest why his result was not very accurate? [$Sn = 119$, $O = 16$.]

2. When lead is heated in air it is turned into a yellow powder, and when the latter is heated with soot, lead is once more obtained. How would the phlogistonists have explained these results?

3. Write a short essay on 'The phlogistic and oxygen theories of combustion.' *Oxf.*

4. With an accurate sketch of the apparatus that was used, describe Lavoisier's famous experiment in which he heated mercury in the air.

Explain clearly the conclusions he drew from the results of his experiment. *Lond.*

CHAPTER 8

THE COMPOSITION OF THE AIR

In the last chapter we considered one of Lavoisier's experiments in which he heated mercury for some days in contact with 50 cub. in. of air, and found that 8 cub. in. disappeared. In the language of to-day we should say that the 50 cub. in. of air contained 8 cub. in. of oxygen, the latter combining with the mercury. According to this, the percentage of oxygen in the jar is only 16. It is actually about 21. Apart from the fact that the experiment is a very cumbrous one, there is another reason, which we shall consider in Chapter 9, why Lavoisier was bound to get a low value for his percentage of oxygen.

You have no doubt seen, or made for yourself, experiments in which the percentage of oxygen was determined. One common method is illustrated in fig. 8/1—the oxygen is removed from the air by means of damp iron filings contained in a muslin bag.

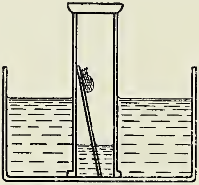

Fig. 8/1

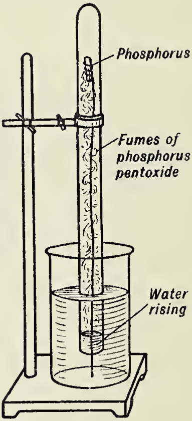

Fig. 8/2. Removing oxygen from air by means of phosphorus

It takes several days to remove the oxygen by this means, but if phosphorus is used instead of iron the process is usually complete in four or five hours. The phosphorus is conveniently held in position by means of a stiff wire.

In both cases it is very important that the nitrogen left at the close of the experiment should be measured at the same temperature and pressure as the original air. The best method is to take the temperature at the beginning of the experiment, to read the barometer, and then 'reduce to N.T.P.' At the end of the experiment a similar correction is applied to the volume of the residual nitrogen. Remember that the pressure of this nitrogen is *not* atmospheric unless, by raising or lowering the jar, the water level inside the jar has been made to correspond with that outside.

Much quicker results are obtained if the phosphorus is allowed to *burn* instead of merely to 'rust' or smoulder. In this case it is placed inside a dry flask or tube closed with a good rubber stopper. After the phosphorus has burnt, the flask is allowed to cool down and is then opened under water. The final result is the same whether the phosphorus has burnt or 'rusted,' showing that there is no essential difference between the two processes. Burning is simply very rapid rusting.

The experiments with iron and phosphorus just described are by no means modern. They were carried out in very much the same way about 1770 by the great Swedish chemist Scheele. We shall meet with him again in connection with the study of chlorine.

As we have seen, the removal of oxygen from the air by means of iron filings is a slow process, and removal by means of phosphorus is not without its dangers. Both these objections are avoided by the use of a substance called pyrogallol. After a solution of this substance in water has been made alkaline with caustic potash it readily absorbs oxygen, turning dark brown as it does so. In carrying out the experiment, the solution of pyrogallol is first poured into the flask

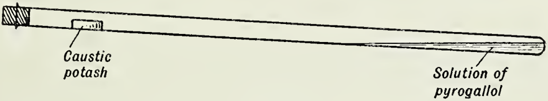

FIG. 8/3

or tube, and a small stick of potash is placed just inside the mouth—away from the solution. The rubber stopper is now inserted and the contents of the tube shaken together, when absorption of oxygen quickly takes place. After two or three minutes the tube is opened under water in the usual way.

For various reasons the methods described are not very accurate. Much better experiments have been devised in which a quantity of air confined over mercury contains a copper spiral which is electrically heated. The copper becomes oxidised, the mercury rises and the volume of the remaining nitrogen can be accurately measured.

More about Nitrogen. We have now considered various means by which atmospheric nitrogen may be obtained. We are, however, left with water in the jar or tube (figs. 8/1 and 8/2), or with pyrogallol solution (fig. 8/3), and to some extent this makes it awkward to examine the properties of the gas. By proceeding as indicated in fig. 8/4 we may obtain jars really full of atmospheric nitrogen and free from carbon dioxide.

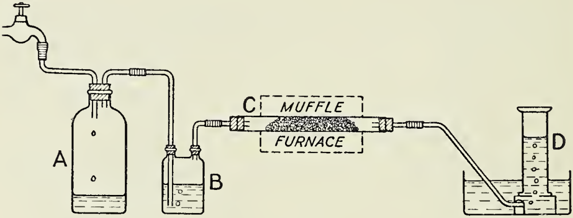

Fig. 8/4

Water from the tap is slowly admitted to the bottle A, driving air into the bottle B containing a solution of caustic soda which removes carbon dioxide. The air then passes through the heated tube C, filled with clean copper turnings, which remove the oxygen. The nitrogen passes on and is collected at D.

It is found to be without colour, smell or taste. It neither burns nor supports combustion, and has no effect on litmus or lime-water. In fact, the properties of nitrogen make up just a bundle of negatives—of things that it will not do. Most gases have some *positive* property—carbon dioxide will turn lime-water milky, oxygen will re-ignite a glowing splint and so on; and this makes them easy to identify. There is, however, no *easy* positive test for nitrogen, and in elementary work we have to assume that a gas is nitrogen if we have proved that it is not one of the other common gases.

Two positive tests, which cannot, however, be described as 'easy,' are the following:

(i) With heated magnesium powder, nitrogen forms a greenish-black compound called magnesium nitride, which reacts with water to form ammonia:—

$$Mg_3N_2 + 3H_2O = 3MgO + 2NH_3$$

(ii) At 0° C. and 76 cm. pressure, nitrogen has a density of 1·257 gm. per litre.

On p. 353 we shall consider a method of preparing nitrogen in which air is *not* used as the source. An important difference between this product, and the 'atmospheric' nitrogen of fig. 8/3, will be discussed later in the present chapter.

Air a Mixture and not a Compound. A great deal of evidence can be given to show that air is a mixture, not a compound. We may select the following:

(1) Although the composition of the air is wonderfully constant, it is not *absolutely* so, as it would be if it were a compound (Law of Constant Composition, p. 24).

(2) The oxygen and nitrogen in air can be partly separated by processes such as would not bring about the decomposition of a chemical compound. Thus

(i) Water dissolves a larger proportion of the more soluble oxygen than of the less soluble nitrogen—proved by the fact that air expelled from solution in water contains a much higher percentage of oxygen than does ordinary air.

(ii) By the action of extreme cold and pressure, air can be liquefied, but the liquid air is richer in oxygen than ordinary air owing to the fact that oxygen is more easily condensed; similarly, when liquid air is allowed to evaporate, the more volatile nitrogen comes off first, and the liquid residue becomes still richer in oxygen.

(3) The properties of a compound are usually very different from those of its constituent elements (e.g. contrast the properties of common salt with those of sodium and of chlorine). The properties of air, however, are exactly what one would expect, knowing those of oxygen and nitrogen. To give just one example, oxygen is a very active supporter of combustion; nitrogen is a non-supporter of combustion; air is a moderately active supporter of combustion.

(4) When two gases combine, heat is produced and there is usually a marked change of volume. But when oxygen and nitrogen are brought together in the proper proportions (oxygen 21 volumes and nitrogen 79), there is neither of these signs of chemical combination, and yet examination shows that air has really been formed.

(5) If air were a *compound* of nitrogen (atomic weight 14) and oxygen (atomic weight 16), it would be possible to express its composition by weight as simple multiples of 14 and 16 respectively; but we cannot do this.[1]

Carbon Dioxide in the Air. You may have noticed that a lime-water bottle often acquires the familiar 'milky' look if it has been standing in the laboratory for a long time, especially if the stopper is not a very good fit. Can there be any carbon dioxide in the air? To answer this question we

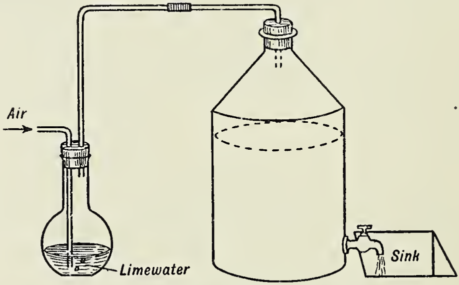

FIG. 8/5. Action of air on lime-water

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[1] In connection with this statement the student should work through Question 2 on p. 91.

place a little clean lime-water in a flask, connected with a 2-gallon aspirator in the way shown in fig. 8/5. As water runs out of the aspirator, the pressure inside the flask is reduced, and fresh air from outside takes its place, passing through the lime-water on its way. Very gradually the lime-water *is* turned milky. This shows that the air contains carbon dioxide, but that the amount present is certainly very small.

How does the carbon dioxide get into the air?

If we 'bubble' through a glass tube into a beaker of lime-water, the latter very quickly turns milky, showing that we breathe out a good quantity of carbon dioxide. This is what happens. The blood contains a substance called hæmoglobin which, in the lungs, combines with oxygen (breathed in), forming oxy-hæmoglobin. This circulates to the tissues, where it meets with impurities which the body must get rid of. These impurities contain carbon, which combines with oxygen from the oxy-hæmoglobin. Thus the carbon becomes carbon dioxide (breathed out), while the oxy-hæmoglobin becomes hæmoglobin once more. It looks as if, in this way, the oxygen of the atmosphere would in time be used up and replaced by carbon dioxide. Fortunately there is a compensating process always at work. In the process of assimilation, plants take in carbon dioxide and give out oxygen. Years ago a boy wrote in an examination paper: 'Suppose you had two flasks connected by glass tubing, and you put a little animal in one flask and a little plant in the other. The animal would take in oxygen and give out carbon dioxide; and the plant would take in carbon dioxide and give out oxygen; and the plant and the animal would go on living in this way for hundreds of years.'

The boy's estimate of the probable length of life seems a little excessive, but he had got hold of the general idea.

Let us look a little more closely into this process of 'taking in carbon dioxide and giving out oxygen.' The plant does this in the process of making sugars such as glucose. Water as well as carbon dioxide is needed, and so is a supply of energy, which is derived from sunlight. We may represent the change by the equation

$$6H_2O + 6CO_2(+\text{energy}) = \underset{\textit{Sugar}}{C_6H_{12}O_6} + \underset{\textit{Oxygen}}{6O_2}$$

The green pigment chlorophyll also plays an essential part, acting as what is called a *catalyst* (p. 145). Because of its dependence on a supply of the energy of sunlight, the process is known as *photosynthesis*.

From sugar, the plant builds up starch (its food reserve), and other compounds that it needs, such as cellulose.

Perhaps we should add here that in the process of respiration (or breathing), a plant also 'takes in oxygen and gives out carbon dioxide.' These results are greatly outweighed, however, by the effect of assimilation already discussed, so on the whole the plant does cause the air to gain oxygen and to lose carbon dioxide.

The air loses and gains carbon dioxide in other ways besides those already mentioned. Thus carbon dioxide is removed not only by the action of plants but also by being dissolved in sea-water, where it serves as food for sea-plants. On the other hand, vegetable and animal matter contain a high proportion of carbon, and when these decay carbon dioxide passes into the air. The same thing happens in the burning of coal. We begin to see that carbon in nature undergoes a round or cycle of changes, the ***carbon cycle***, as it is called. Let us sum up, beginning with carbon dioxide.

(i) This, together with water, is turned by plants into sugar, and thence into starch and other carbon compounds, with *intake* of energy from sunlight.

(ii) Plant products, including starch, taken as food are turned into carbon dioxide and breathed out. They may also be turned into carbon dioxide by ordinary burning (perhaps after slow conversion into coal) or by decay. In any case, we get back to the carbon dioxide with which we started, and by whatever process the carbon dioxide is produced, its formation is accompanied by *output* of energy (as heat). Our balance-sheet has to take account not only of gains and losses of oxygen and carbon dioxide, but also of gains and losses of energy.

The carbon cycle is accompanied by an *oxygen* cycle, for oxygen is given out in (i) and used up in (ii). There is a nitrogen cycle also. We are hardly in a position to understand the details yet, but we will consider the matter later (Chapter 32).

Air dissolved in Water. You have often noticed that when you begin to heat a beaker of water, bubbles soon begin to form round the sides and bottom. These bubbles consist of air which the water had dissolved. We may collect this air by using the apparatus sketched in fig. 8/6. The flask and delivery tube must both be quite *full* of water to begin with, otherwise some of the gas collected in the tube T will be simply ordinary air, and not air which has been dissolved in water.

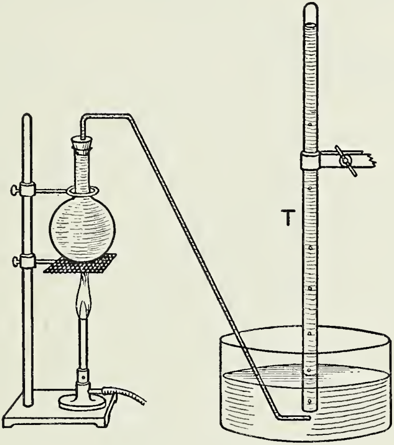

FIG. 8/6. Expelling dissolved air from water

The best way to go to work is to take the delivery tube with cork attached, and dip the 'cork' end into a beaker of water. Fill with water by suction, and you will find that you can put your finger on the other end while it is still in your mouth. Keeping your finger tightly over the end, push the cork gently into the flask, which has been previously filled with water. Now remove your finger and push the cork in tightly. In fig. 8/6 notice that the delivery tube does not project below the narrow end of the stopper. This is to prevent any of the air expelled on heating from lodging under the stopper.

By filling the flask again and again, we can obtain enough of the air to analyse by any of the simple methods previously described (say by the 'pyrogallol' method), when it will be found that the percentage of oxygen is much higher than in ordinary air—36 per cent. or so, instead of 21.[1] In fact, it is said that this air will sometimes re-ignite a glowing splint. The higher percentage of oxygen is due of course to the fact that it is more soluble than nitrogen, and the result has already been quoted as evidence that air is a mixture and not a compound. The dissolved oxygen is essential to the life of fish.

Water-vapour in the Air. Water is constantly evaporating into the air, with the result that air always contains more or less water in the form of an invisible vapour. Its presence may be shown in various ways. A simple method consists in polishing a beaker so as to make it perfectly dry on the outside, and then putting some ice inside it. Water soon condenses on the outside surface. We may prove that the liquid *is* water by touching it with a fragment of copper sulphate (blue vitriol) which has been 'dehydrated,' i.e. gently heated so as to make it lose its water of crystallisation. When dehydrated the copper sulphate becomes white, but it resumes its blue colour when brought into contact with water.

Larger quantities of water may be obtained from the air by exposing some calcium chloride (contained in an evaporating dish) for a few days. The calcium chloride absorbs so much water that it becomes semi-liquid, or it may even dissolve completely in the water which it has absorbed. The wet substance is now transferred to a flask attached to a Liebig's condenser (fig. 8/7), and pure water is obtained by distillation.

Incidentally we may notice that a substance which will absorb atmospheric moisture is said to be *hygroscopic*. It may or may not become wet in the process. If it does, we say that it is *deliquescent*. Evidently a deliquescent substance is necessarily hygroscopic, but a hygroscopic substance may not be deliquescent. Other examples of deliquescent substances (besides calcium chloride) are caustic soda and copper nitrate.

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[1] If the water contains calcium bicarbonate ('temporary hardness,' p. 181), this will decompose on heating, and the gas collected may contain a large proportion of carbon dioxide, though the latter formed only a very small part of the dissolved air. To get over the difficulty, the air should be collected over a solution of caustic potash instead of over water.

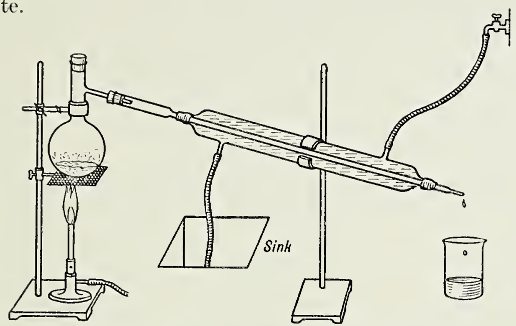

FIG. 8/7. Distilling wet calcium chloride

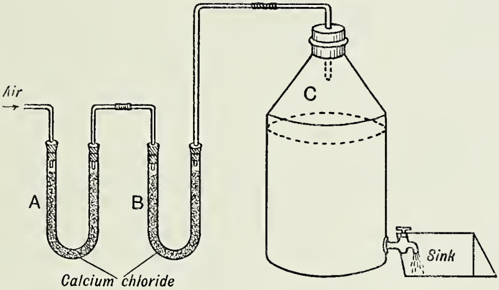

FIG. 8/8. Finding amount of water-vapour in air

The amount of water-vapour in the air is usually found by indirect means, which are described in books on Physics. It may be found, however, by the following direct process.

A and B are U-tubes containing calcium chloride (or better, pieces of pumice stone soaked in concentrated sulphuric acid). They are connected with a large aspirator C as shown in fig. 8/8.

The aspirator is filled, and A and B are weighed. Water is then slowly run out of the aspirator, with the result that a slow current of air is drawn through A and B. After a measured quantity of water, say 5 litres, has been run out, A and B are weighed again. The increase in the weight of A gives us the weight of water contained in 5 litres of air, and we can easily calculate the amount present in any given volume.

The object in weighing B is to make sure that A is doing its work properly. If B shows no increase in weight, we know that all the water-vapour has been arrested by A.

Other Constituents of the Atmosphere. Besides oxygen, nitrogen, carbon dioxide and water-vapour, air contains only one other constituent in considerable quantity—a gas called argon. The story of argon is a curious one and begins with the year 1785. By that time the fact that air consists chiefly of oxygen and nitrogen was well known, Priestley and Lavoisier having carried out their famous experiments a few years earlier. Nitrogen, however, was usually called phlogisticated air, and oxygen dephlogisticated air.

In the year 1785 a great chemist named Henry Cavendish was carrying out some experiments with the object of turning 'phlogisticated air' into nitre (potassium nitrate). His method was to pass electric sparks through air contained in a tube which stood over caustic potash. This caused the oxygen and nitrogen to combine little by little, forming oxides of nitrogen; and as fast as these oxides were produced they were absorbed by the caustic potash, forming potassium nitrate.

There is not nearly enough oxygen in the air to combine with all the nitrogen, so Cavendish kept adding more oxygen, and sparking, until he felt sure that the nitrogen had had every chance to be used up. He then introduced a solution of 'liver of sulphur' (potassium sulphide) into the tube from below, to absorb all the surplus oxygen, and, believing that all gases had now been removed, he expected that the caustic potash plus liver of sulphur solution would rise to the top. It did—very nearly. One little bubble of gas, however, remained at the top. Thinking this was 'phlogisticated air,' he repeated the process of adding oxygen, sparking and absorbing, but still this obstinate little bubble remained. Most of us would have put it down cheerfully as 'due to impurities' or something of the sort, but the careful Cavendish measured the bubble as well as he could, and left it on record that 'if there be any part of the dephlogisticated air of our atmosphere which differs from the rest and cannot be reduced to nitrous acid, we may safely conclude that it is not more than 1/120 part of the whole.' On p. 90 there is a facsimile of part of his original notes on the subject.

More than a hundred years later—in 1894—there was a sequel. Sir William Ramsay and Lord Rayleigh were carrying out some experiments with nitrogen, and found that when they obtained their nitrogen from the air (removing the oxygen by means of heated copper) it was always a little heavier than when they obtained it in other ways. The difference was not very great—about a half of 1 per cent.—but it made them suspect that 'atmospheric nitrogen' really contained a small proportion of some heavier gas.

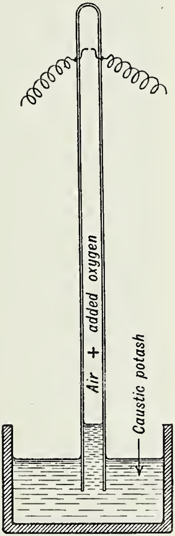

Fig. 8/9. Cavendish's experiment

By various ways—one of them was really Cavendish's old method, but with much improved apparatus—'atmospheric' nitrogen was treated in such a way as to remove the real nitrogen. It was found that, starting with 100 c.c. of dry air, the final yield of argon[1] (as they called the new gas) was 0·933 c.c., so Cavendish was not far out when he spoke of a '1/120 part.'

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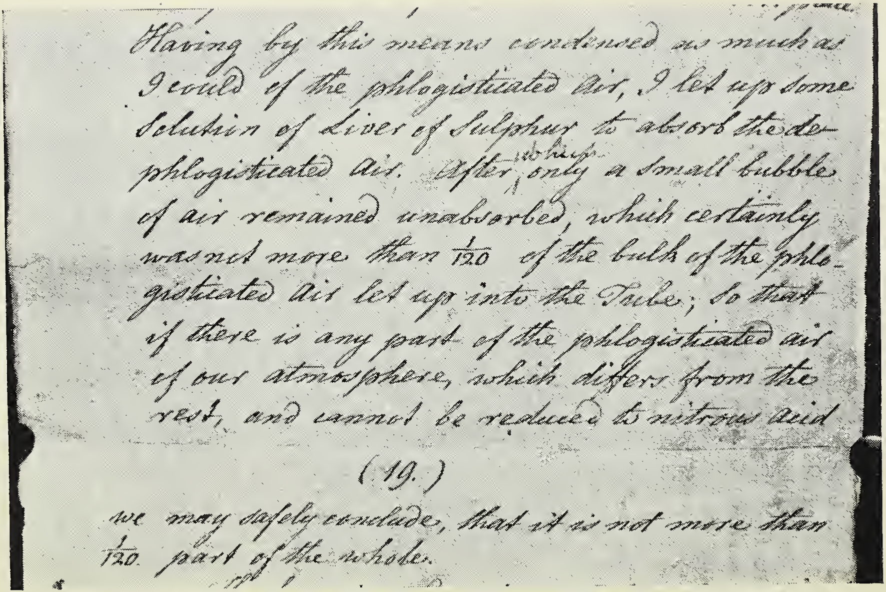
[1] 'It was first named *aeron* to denote its connection with the atmosphere, but its discoverers received so many letters inquiring when Moses might be expected to turn up that they finally rechristened it *argon* (from a Greek word meaning *lazy*) in order to avoid confusion.'—Professor Kendall in *At Home Among the Atoms.*



Having by this means condensed as much as I could of the phlogisticated Air, I let up some Solution of Liver of Sulphur to absorb the dephlogisticated Air. After which only a small bubble of air remained unabsorbed, which certainly was not more than $\frac{1}{120}$ of the bulk of the phlogisticated Air let up into the Tube; so that if there is any part of the phlogisticated air of our atmosphere, which differs from the rest, and cannot be reduced to nitrous acid

(19.)

we may safely conclude, that it is not more than $\frac{1}{120}$ part of the whole.

Facsimile of an extract from notes written by the Hon. Henry Cavendish in 1785

Argon is an extremely *inert* gas, showing no tendency to take part in chemical action of any sort. Its atoms do not combine even with one another (contrast with oxygen, hydrogen, nitrogen, etc., where the atoms have combined to form pairs, O_2, H_2, N_2, etc.). In other words, its *atomicity* (p. 124) is one. Certain uses have been found for it. Thus it is used as a filler for half-watt lamps. It is found that if the tungsten filament is surrounded with argon instead of with a vacuum, it can be made much hotter without blackening the bulb. It is also used in the extraction of titanium, and in certain arc-welding processes.

It may be of interest to add that having discovered argon, Ramsay continued his researches, and in the next few years isolated from the air a whole group of inert gaseous elements, including neon, krypton and xenon. They are present only in very tiny amounts, e.g. krypton, about one part in a million parts of air, and xenon about one part in 20 millions. As a filler for electric lamps krypton is more efficient than argon, but because of its high cost is used only in rather special cases (e.g. for miners' cap-lamps). Neon gives a beautiful orange-red glow when an electric discharge is passed through it at low pressures, and for this reason is used in making advertisement signs.

Questions

1. In 1841 Dumas and Boussingault passed air over heated copper, collecting the unchanged nitrogen in a vacuous flask, previously weighed. The weight of the nitrogen was thus found to be 12·373 gm., and the oxygen with which it had been mixed caused the copper to gain in weight by 3·680 gm. Find the percentage of oxygen and nitrogen in the air *by weight.*

2. Air contains 23·2 per cent. of oxygen by weight, and 75·5 per cent. of nitrogen (the remaining 1·3 per cent. being chiefly argon). Working by the method explained on p. 49, find what its simplest formula would be *if* the nitrogen and oxygen were combined. To what conclusion does your answer lead you? ($O=16$, $N=14$.)

3. Into a graduated tube containing 80 c.c. of air which had been expelled from water a piece of phosphorus was introduced as in fig. 8/2. The water rose 28 c.c. Calculate the percentage of oxygen in the sample of air, and comment on the value obtained.

4. Describe carefully how you would determine, to within about 1 per cent., the percentage by volume of oxygen in a sample of ordinary air. Draw a diagram to show how you would take your measurements of volume. Explain why this experiment cannot be done satisfactorily by burning a candle in a measured volume of air. *Camb.* (*part*)

5. Give your reasons for believing or disbelieving that air is a mixture. *J.M.B.* (*part*)

6. Name *two* common gases, other than nitrogen and water vapour, which are normally present in air.

Describe, giving necessary experimental details, how you would prove the presence of each of these gases in the air. *Oxf.*

7. As a result of the breathing of animals, and in other ways, carbon dioxide is constantly passing into the atmosphere. What are these 'other ways'? How is it that the percentage of carbon dioxide does not increase?

8. Draw a diagram of the apparatus you would use to demonstrate that when water which has been exposed to the atmosphere is boiled, gases other than steam are evolved. How would you show that the composition of this gas mixture differs from that of ordinary air? Explain the importance of these gases in solution to aquatic animals and plants. *Camb.*

9. The atmosphere is said to contain water-vapour. How would you obtain and collect a sample of water *from the atmosphere*? How would you prove this water to be pure? *J.M.B.* (*part*)

CHAPTER 9

WATER

Perfectly pure water is a substance never met with in everyday life and very seldom even in the laboratory. The reason is that water possesses such extraordinary powers as a *solvent*. Even before it reaches the ground, rain will have dissolved carbon dioxide (and some of the other gases) out of the air, and once in contact with the earth it will begin to dissolve out many different solid substances. Some of these we shall consider when we come to the subject of 'hard water' in Chapter 16.

In the laboratory we often need water that shall be as free as possible from dissolved matter, and to secure this the water is submitted to *distillation*, a double process which consists in boiling the water to turn it into steam, and then cooling the steam to turn it back into water. The solid impurities remain behind in the flask in which the water was boiled. A *Liebig's condenser* is usually employed, the cooling being secured by surrounding the vapour tube with an outer jacket through which there circulates a current of cold water (see fig. 8/7 on p. 87).

Action of Water on Metals. Many metals act upon water with the liberation of hydrogen. The temperature required depends upon the metal. Thus iron must be made red-hot, while water in the form of steam is passed over it. In the case of potassium a temperature of 0° C. is sufficient—potassium will actually liberate hydrogen from ice!

We will now consider these reactions in some detail.

Sodium. This acts very vigorously on cold water. The heat produced is sufficient to melt the metal, which rushes about on the surface as a molten ball (sodium is lighter than water).

$$[Na + H_2O = NaOH + H]$$
$$2Na + 2H_2O = \underset{\text{Sodium hydroxide}}{2NaOH} + H_2$$

Ordinarily the hydrogen does not take fire, but does so if the sodium is prevented from rushing about (e.g. by floating it on a piece of filter-paper).

To *collect* the hydrogen, it is best to wrap up the sodium—a fragment about the size of a pea is sufficient[1]—in a piece of lead-foil, the latter being pierced with a few pin-holes so that the water can get at the sodium. The gas is easily collected in a test-tube as illustrated in fig. 9/1.

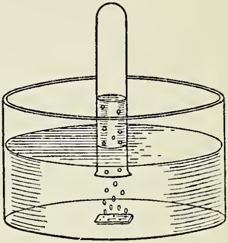


FIG. 9/1
Action of sodium on water

The liquid now turns litmus paper blue and feels soapy when rubbed between the fingers. It consists of a solution of sodium hydroxide, and on boiling down, the latter is easily obtained as a deliquescent solid (if you have forgotten the meaning of 'deliquescent,' turn back to p. 87).

Potassium (another very light metal) acts similarly, but with even greater vigour ($2K + 2H_2O = 2KOH + H_2$). If the metal is allowed to float on the water, the heat produced by the chemical action is so great that the gas takes fire, the flame being coloured violet owing to the presence of potassium. Potassium hydroxide may be recovered from the solution as already described.

Calcium is much easier to manage than either of the metals just mentioned. It sinks in water, and the hydrogen is readily collected by some such arrangement as that shown in fig. 9/2. The action slows down before long, because the pieces of calcium become coated with the comparatively insoluble calcium hydroxide[2]:—

$$Ca + 2H_2O = Ca(OH)_2 + H_2$$

From this equation you can easily see why calcium must be kept in a well-stoppered bottle.

---

[1] Some nasty explosions have resulted from the use of large pieces.

[2] Avoid the common mistake of writing $Ca + H_2O = CaO + H_2$.

Magnesium. This metal, even in the form of filings, is acted upon only very slowly by cold water. However, with the arrangement shown in fig. 9/3 a test-tube of hydrogen may be collected in the course of a day or so. It will be seen that the cork serves to keep the filings in position, while the displaced water can escape through the short open tube. The equation is

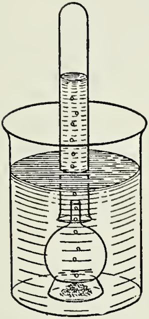


FIG. 9/2. Action of calcium on water

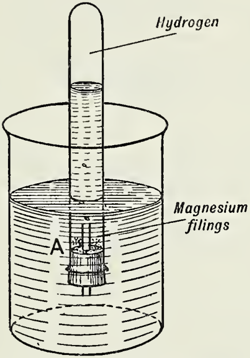


FIG. 9/3. Action of magnesium on cold water

$$Mg + H_2O = MgO + H_2$$

Magnesium oxide is only very slightly soluble (forming the hydroxide $Mg(OH)_2$), but the solution at A is strong enough to turn a piece of litmus paper blue.

If magnesium is heated in a current of steam, the action is very vigorous. The apparatus shown in fig. 9/4 may be used. Magnesium filings are placed in the deflagrating spoon, the attached wire of which (somewhat shortened) is slightly bent so as to make it grip the inside of the glass tube. The filings are heated with a bunsen till they just begin to burn and are then plunged into the steam, the water having been previously made to boil briskly. The magnesium continues to glow brilliantly in the steam, and hydrogen is rapidly given off.

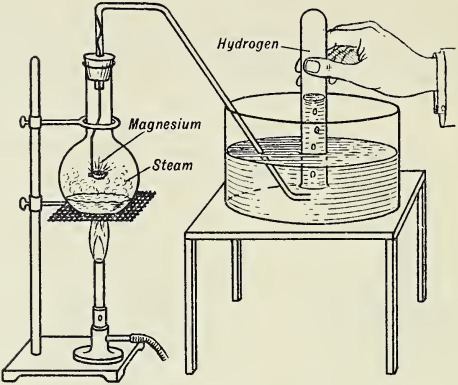


FIG. 9/4. Action of magnesium on steam

Iron. If asked to describe the action of water on iron, be careful to avoid saying that it causes it to rust. Water does not rust iron unless air is also present.

Heated iron, however, like magnesium, is acted upon by steam—the experiment will be sufficiently indicated by

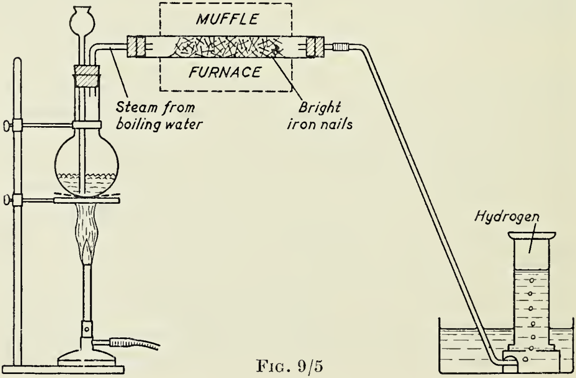


FIG. 9/5

fig. 9/5. At the close of the experiment the bright iron nails are found to be coated, not with ordinary brown rust, but with a greyish black rust known as *triferric tetroxide*:—

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$

The nails should be weighed before and after the experiment, and will be found to have increased in weight.

Copper. There is no action, even if the metal is made white-hot as the steam passes over it. This resistance to the action of steam makes copper a particularly suitable metal for the condenser tubes of locomotives.

The Case of Iron Further Considered. We have seen that if steam is passed over heated iron, iron oxide and hydrogen are produced. If, however, we reverse the experiment by passing hydrogen over heated iron nails, we find that iron and steam are obtained. To prove this, it is evidently important to be sure that there was no steam mixed with the hydrogen until it had passed over the oxidised nails. In practice, the generating flask A tends to become rather hot, and a considerable amount of water-vapour passes over with the hydrogen. Much of this vapour condenses in the cooled flask B, and the rest of it is absorbed by the series of calcium chloride tubes, the last of which should show no increase in weight at the close of the experiment. By that time, the cooled U-tube C will be found to contain some water (for tests, see p. 107), and the nails will be found to have lost the weight they had gained in the first of the two experiments.

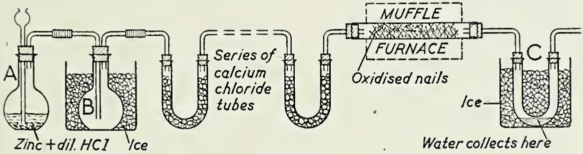


FIG. 9/6

Expressing our results as equations, we have

$$(A)\ 3Fe + 4H_2O = Fe_3O_4 + 4H_2$$
$$(B)\ Fe_3O_4 + 4H_2 = 3Fe + 4H_2O$$

This is a good example of a *reversible reaction*, and the subject is so important that we must consider it in some detail.

Suppose our iron and steam are both enclosed in a heated porcelain bomb, and let us trace out what will happen. At first there is obviously only one thing that *can* happen—the change represented by equation *A* above. Iron oxide (Fe_3O_4) and hydrogen will begin to be produced. As soon as even a little of these substances has been produced, change *B* will set in, so that both *A* and *B* will now be in operation. But (at this early stage) *B* will not go on nearly so rapidly as *A* simply because the materials necessary for reaction *B* are not present in nearly such large quantities as those required for reaction *A*.

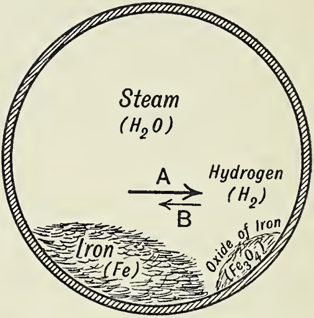


Fig. 9/7. Action of steam on iron, early stage (diagrammatic only)

But as time goes on these materials (for reaction *B*) increase in amount, with the result that this reaction goes on at an ever-increasing rate. Further, the materials required for reaction *A* are steadily diminishing in amount, so that this reaction is all the time slowing down. We begin to see what will happen. *A point will be reached at which reaction A and reaction B will both be going on at the same rate.* From that time forward, if it were possible to make analyses of the contents of the bomb at intervals of, say, five minutes, we should find no change whatever in the quantities of each of the four substances present—*not* because no chemical change is taking place, but because *two opposite chemical changes are going on at equal rates.* Such a condition of things is known as a state of ***chemical equilibrium***, and the reversible reaction is said to be ***balanced***. This balance will be maintained so long as the temperature remains constant. An increase of temperature would speed up both reactions, but not to the same extent. Actually it would speed up *B* more than *A*, and the equilibrium would be disturbed. What happens next? Simply because *B* is going on faster than *A*, iron and steam will be produced at a greater rate than iron oxide and hydrogen. Thus the iron and steam will increase in amount, while the hydrogen and iron oxide will diminish. This causes *A* to speed up and *B* to slow down, until *A* and *B* are once more going on at the same rate and a new condition of equilibrium is set up—*new*, because there would obviously be more iron and steam, and less hydrogen and iron oxide than were present in the equilibrium first considered. So long as the temperature remains constant, however, the quantities of each of the four substances will remain constant at their new values.[1]

If the reader has difficulty in grasping the idea of equilibrium[2] he may find the following illustration helpful. A boy is on his bicycle in the country and has to get off on account of a puncture. Hoping that it will not be necessary to mend it on the spot, he begins to pump up. That stands for reaction *A*—air is going in. The reverse action *B* (escape of air through the puncture) is non-existent at first, but it sets in as soon as a little air has entered the tube. As the boys gets tired, *A* slows down (*i.e.* the air entering per second becomes less and less), while, owing to the rise of internal pressure, *B* increases. If the puncture is at all large, there will be a melancholy state of equilibrium while the tyre is still only partly 'up'—a third perhaps, or half, three-quarters, etc.,—the state of equilibrium depending on the size of the puncture and on the speed with which the boy pumps.

For purposes of discussion we have supposed the iron and steam to be in a closed bomb, and we came to the conclusion that all four substances (iron, steam, iron oxide, and hydrogen) would finally be present, because reaction *A* and reaction *B* are *both* going on. If, however, we pass steam over heated iron in a tube, *only A can go on*; because to make B possible, hydrogen must be present—and here the hydrogen is swept away in the current of steam as fast as it is formed. Thus reaction *A* 'goes to completion,' as we say.

---

[1] Experiments illustrating reversible reactions are described on pp. 208–210 of the author's *School Course of Practical Chemistry* (Bell).

[2] The idea of equilibrium is so important—not merely in chemistry, but in many other directions—that it is well worth taking a little trouble to grasp it. Though not very difficult, it is not so easy that it can be acquired by a quick casual reading, or by lazy thinking.

Similarly, if hydrogen is passed over heated iron oxide, reaction *B* goes to completion, because the steam necessary for reaction is constantly being swept away. For the reaction to become balanced, conditions would have to be such that none of the reacting substances could escape.

The reactions just discussed are carried on industrially for the preparation of pure hydrogen (99% or more) used in the treatment of oils and soft fats (p. 4). Spongy iron is employed so as to present a large surface, and when the iron has been oxidised, water gas ($H_2 + CO$) is passed over the product to reconvert it into iron. Thus there is a regular alternation of the two processes, oxidation and reduction.

Reversible reactions are very common indeed. We have an interesting example in the case of Lavoisier's experiment on the heating of mercury in an enclosed volume of air (p. 78). You may remember that he had 50 cub. in. of air in the jar, and only 8 cub. in. of this combined with the mercury, although the experiment was continued for nearly a fortnight. Now as one-fifth (rather more) of the air by volume consists of oxygen, we should have expected 10 cub. in. to combine with the mercury. Try to account for Lavoisier's result—he was much too careful a worker to have made a mistake of 2 cub. in. in his measurement.

Another simple example of a reversible reaction is the heating of limestone or chalk, $CaCO_3 \rightleftharpoons CaO + CO_2$. (Notice the sign $\rightleftharpoons$ used to express such a reaction.) The reactions would reach a state of balance if the limestone were heated at a constant temperature in an enclosed space. Actually, of course, the limestone 'burner' is not interested in the reverse action ($CaO + CO_2 = CaCO_3$), except to reduce it as much as he can, which he does by arranging for the carbon dioxide to escape as fast as possible.

In Chapter 28 we shall be considering the reversible reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$—the combination of nitrogen and hydrogen to produce ammonia. In this case the unwanted reverse action ($2NH_3 = N_2 + 3H_2$) is discouraged by the rapid removal of the ammonia, either by liquefying it or by dissolving it in water.

Electrolysis of Water. So far we have not considered any experiment in which water has been decomposed in a straightforward way into oxygen and hydrogen. We have frequently obtained the latter, but the oxygen has always attached itself to the metal—it has never come out into the open, so to speak. A good way of obtaining the oxygen is by what is called the 'electrolysis of water,' i.e. the decomposition of water by means of an electric current.

The experiment is usually carried out in a 'Hoffmann's Voltameter.' This consists of a U-tube with two long arms, A and B, while a third tube C, slightly taller than A or B, runs into the bend which joins them. To fill the tubes we pour water into C until it rises to the taps T_1 and T_2, which are then closed.

E_1 and E_2 are two pieces of platinum-foil known as ***electrodes.*** They are soldered to platinum wires which are fused through the glass sides of the tubes and are then connected with the terminals of an electric battery usually consisting of three or four Daniell cells.

If the liquid between E_1 and E_2 will conduct electricity, the circuit will be complete, and the idea is that as the current passes through the water it will decompose it, and that oxygen will collect at one electrode, say E_1, and hydrogen at the other, E_2. From them the gases will rise into A and B respectively.

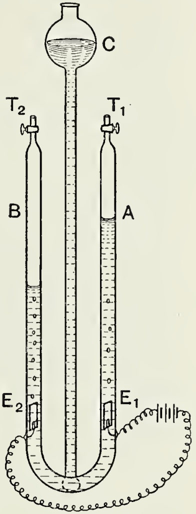


Fig. 9/8
Electrolysis of water

Unfortunately, water does *not* conduct electricity, and what happens is just—nothing.

On adding about a thimbleful of sulphuric acid to the liquid, however, bubbles of gas immediately collect at E_1 and E_2, and soon begin to rise into A and B. When tested, the gases are found to be oxygen and hydrogen, and the volume of the hydrogen is found to be twice that of the oxygen.

Later on you will learn something more about the action of the sulphuric acid. For the present we may take it that it simply enables the water to conduct electricity. It is still present at the close of the experiment, so that we shall not be far wrong in concluding that the water alone has been decomposed into two parts (by volume) of hydrogen and one of oxygen.

Volumetric Composition of Steam. In our last experiment we measured the volume of the hydrogen and the oxygen, but not of the water. Indeed, there would be little point in doing so, because we should be measuring the volume of a *liquid* in one case and of two *gases* in the other, and we could hardly make a fair comparison. In the following experiment, however, the temperature is kept at above 100° C. throughout, so that the water is in the form of a gas, i.e. steam.

ABC is a U-shaped tube, with tap, made of rather stout glass so as to stand the shock of a moderate explosion. The closed limb contains a mixture of hydrogen (2 vols.) and oxygen (1 vol.) confined over mercury. The mixture is usually obtained by the electrolysis of water as shown in fig. 9/9*a*.

The closed limb is surrounded by a wider tube through which there circulates the vapour of a liquid boiling at a temperature well above 100°. (Amyl alcohol, b.p. 130°, is often used.) Mercury is run out of the other limb, or poured into it, until the liquid stands at the same height in both limbs. The 'gas' column is divided by rubber bands into three equal parts.[1] A spark is then passed, but before doing so an extra quantity of mercury is first poured into the open limb and the end is firmly closed by the thumb. These precautions prevent mercury from being flung out by the explosion.

Mercury is now added (or withdrawn) until it again stands at the same level in both tubes. It will be found that the volume of gas has contracted from three volumes to two.

---

[1] A preliminary experiment is necessary to ascertain the position of the bottom ring, but the present description is intended to be only a general one.

When the current of vapour is stopped and the closed limb of the tube is allowed to cool, it will be found that the mercury rises to the top. This shows that all the hydrogen and oxygen

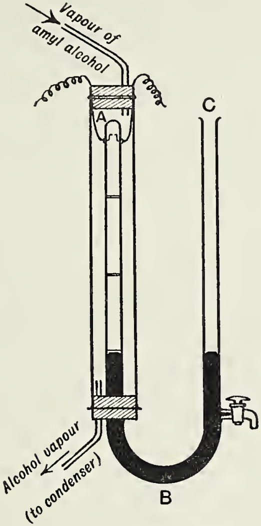


Fig. 9/9. Volumetric composition of steam

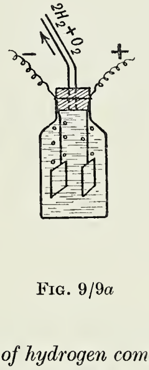


Fig. 9/9*a*

has been used up. Thus *two volumes of hydrogen combine with one volume of oxygen, forming two volumes of steam.*

Notice that all volumes are measured at the same pressure (atmospheric), and that the temperature is constant throughout.

The Formula for Water. The result of the last experiment is very important, because by means of it we can show that water (or, to be quite accurate, steam) has the formula H_2O. For convenience we will give the proof now, though you will have to postpone the reading of it until you have studied Avogadro's Hypothesis (Chapter 11).

Suppose 1 vol. of hydrogen contains x molecules.

$\therefore$ 1 vol. of oxygen contains x molecules and so does 1 vol. of steam (Avogadro's Hypothesis). Now

2 vols. hydrogen + 1 vol oxygen = 2 vols. steam (experiment).

$\therefore$ $2x$ molecules hydrogen + x molecules oxygen
= $2x$ molecules steam.

Dividing throughout by $2x$, we have

1 molecule hydrogen + $\frac{1}{2}$ molecule oxygen = 1 molecule steam.

Now the molecule of hydrogen contains 2 atoms (p. 124) and so does the molecule of oxygen.

$\therefore$ 2 atoms hydrogen + 1 atom oxygen = 1 molecule steam.

Since the molecule of steam consists of 2 atoms of hydrogen combined with 1 of oxygen, its formula must be H_2O.

This is confirmed by the fact that the vapour density of steam is 9 (see p. 126). Its molecular weight is therefore 18, a result which agrees with the formula.

Notice that we cannot work out the formula for water from the results of our *electrolysis* experiment. Let us see how far we can get.

2 vols. of hydrogen + 1 vol. of oxygen
= (quantity of water unknown)

$\therefore$ $2x$ molecules of hydrogen + x molecules oxygen = ?

Before, we divided throughout by the number of molecules of steam ($2x$) and so found the composition of a single molecule. *Now,* we do not know what to divide by. All we can conclude is that water is made up of hydrogen and oxygen in the proportion of 2 molecules to 1 molecule respectively, i.e. its formula is to be chosen from H_2O, H_4O_2, H_6O_3 . . . etc., but we do not know which to select.

Finally, note that our proof (from the 'explosion' experiment) applies only to *steam.* When this condenses to water we are faced with the uncertainty just mentioned. In fact, there is strong evidence that liquid water (not steam) is actually a mixture of several kinds of molecules, H_2O, H_6O_3, H_8O_4, and possibly some others.

Water of Crystallisation. When copper sulphate crystallises out from its solution in water, it is found that the crystals have the formula $CuSO_4.5H_2O$. Compounds like this are very common, i.e. compounds in which one molecule of a salt is combined with a definite number of molecules of water known as ***water of crystallisation***, or ***water of hydration.*** On heating, this water is easily driven off, and we are left with what is called the ***anhydrous salt.*** A few common examples of salts containing water of crystallisation are—

Washing soda, $Na_2CO_3.10H_2O$ (hydrated sodium carbonate)
Glauber's salt, $Na_2SO_4.10H_2O$ (hydrated sodium sulphate)
Epsom salt, $MgSO_4.7HO_2$ (hydrated magnesium sulphate)

It is found that these 'hydrates,' or 'salt hydrates,' sometimes lose part or all of their water of crystallisation simply by exposure to a dry atmosphere.[1] The residue usually has a powdery, floury appearance, and we say that the substance has ***effloresced.*** Thus crystals of washing soda often effloresce, and the crystals become covered with a powdery substance having the formula $Na_2CO_3.H_2O$. Glauber's salt is also efflorescent.

In passing we may notice that a salt often holds its last molecule of water of crystallisation much more tenaciously than the others. The name 'water of constitution' has sometimes been given to this last molecule, because it is suggested that it is perhaps combined with the 'salt' molecule in a specially intimate way.

It must not be thought that all salts contain water of crystallisation. Sodium chloride, $NaCl$, and silver nitrate, $AgNO_3$, contain none, and many others might be mentioned, including all common salts of potassium and ammonium, e.g. potassium nitrate, KNO_3, potassium chlorate, $KClO_3$, and ammonium sulphate, $(NH_4)_2SO_4$.

Number of Molecules of Water of Crystallisation. By a very simple experiment we can often find the number of molecules of water of crystallisation present in a given salt. A quantity of the substance is first weighed, and then heated in a crucible until all the water has been driven off. We now weigh again, and work out our results as shown in the following example. The substance used is supposed to be hydrated copper sulphate, $CuSO_4.xH_2O$, where x has to be found.

---

[1] Hydrated cobalt chloride, $CoCl_2.6H_2O$, gives a pink solution, and words written with it are practically invisible ('invisible ink'). On warming the salt, the anhydrous chloride, $CoCl_2$, is produced, and the characters stand out in clear blue, fading out again as the paper cools and more moisture is absorbed from the atmosphere.

(*a*) Wt. of empty crucible	13·72 gm.
(*b*) Crucible + copper sulphate (before heating) .	18·83 ,,
(*c*) Wt. after heating	16·99 ,,
∴ wt. of hydrated copper sulphate . . . =	5·11 ,,
and loss of weight (from 5·11 gm. hydrated sulphate) =	1·84 ,,

∴ 1 gm. of hydrated sulphate loses $\frac{1{\cdot}84}{5{\cdot}11}$ gm.

If now we write down the equation and fill in the atomic weights we have

$$\begin{array}{ccc} Cu\ \ S\ \ O_4\ .\ xH_2O & = Cu\ \ S\ \ O_4 & +\ xH_2O \\ \underbrace{64+32+64+x(2+16)}_{160+18x} & \underbrace{64+32+64}_{160} & \underbrace{x(2+16)}_{18x} \end{array}$$

i.e. $(160+18x)$ gm. hydrated sulphate loses $18x$ gm. water,

∴ 1 ,, ,, ,, $\frac{18x}{160+18x}$ water.

We now have

by *experiment* 1 gm. loses $\frac{1{\cdot}84}{5{\cdot}11}$

,, *equation* 1 gm. ,, $\frac{18x}{160+18x}$.

These must be equal.

$$\therefore \frac{1{\cdot}84}{5{\cdot}11}=\frac{18x}{160+18x}.$$

Working out, we obtain $x=5{\cdot}00$.
Thus the formula is $CuSO_4.5H_2O$.

In carrying out experiments such as the above, the following points should be kept in mind.

1. Heat *very gently* at first and with the crucible lid almost completely covering. Crystals often fly about if heated violently at first, owing to the sudden conversion of their water of crystallisation into steam within the crystal.

2. Even at the later stages the dehydrated substance sometimes undergoes further change if the heating is very strong, e.g. (p. 466) copper sulphate gives a basic sulphate. In most cases complete dehydration (without further complications) will be secured by placing the crucible about an inch above the top of a bunsen flame turned full on. Heat for about 20 minutes.

3. Cool in a desiccator—these dehydrated substances are usually hygroscopic—and weigh with the lid on.

4. Finally, heat for another five minutes, cooling and weighing with the same precautions as before. *There should be no further change in weight.* If there is, it will, of course, be necessary to heat again until a constant weight is obtained.

This additional heating and weighing must be carried out in all cases where a quantitative chemical change is being brought about by the action of heat; otherwise there is no guarantee that the change is complete.

Tests for Water. A liquid is water if it

(1) is without colour or smell,
(2) boils at 100° C.,
(3) freezes at 0° C.,
(4) has a density of 1 gm. per c.c.,
(5) causes dehydrated copper sulphate to become green or blue.

A little thought will show that the above tests do not prove that the water is *pure.* Water containing, for instance, just a little common salt in solution, or a little acid, would answer to all the above tests as ordinarily carried out.

Thoroughgoing tests for the purity of water—its freedom from typhoid germs, for instance—would carry us far beyond the scope of this book. The following tests are sufficient for most cases arising in the ordinary work of the laboratory:

(1) The liquid should leave no residue on evaporation.

(2) It should be neutral to litmus.

(3) It should remain quite clear on adding barium chloride, silver nitrate, and Nessler's solution to successive portions.

Barium sulphate, barium carbonate and silver chloride are all highly insoluble in water. Hence, if there is no cloudiness we know that sulphates, carbonates and chlorides—very common impurities in 'tap-water'—are absent. The test is a much more severe one than the apparent absence of residue on evaporation.

Nessler's solution is a very delicate reagent for ascertaining the presence of ammonium salts. If these are present it turns brown.

On the question of lead as an impurity in drinking water, see pp. 471 and 476.

History. Water was one of the four elements of the Greeks, the other three being earth, fire and air.[1] Traces of this ancient idea are seen in such phrases as 'the raging of the elements.' That Priestley had no doubts on the subject is evident from the last few words of the following passage which he wrote in 1774 with reference to air: 'There are, I believe, very few maxims in philosophy that have laid firmer hold upon the mind than that air . . . is *a simple elementary substance*, indestructible, and unalterable, at least so much as water is supposed to be.'

Now Priestley was not (like Lavoisier) a man who first did a great deal of hard thinking, arrived at a conclusion and then carried out experiments to find whether his conclusions were right or wrong. He was an experimenter *first*, and many of his discoveries were made by very haphazard methods. We have seen how his discovery of oxygen (1774) enabled Lavoisier to unravel the problem of the composition of the air and the nature of combustion. In 1781 another of his experiments gave Cavendish a hint which led to the discovery of the composition of water. Priestley had made what he called 'a random experiment' for the entertainment of a few of his scientific friends. It consisted in exploding, by means of an electric spark, a mixture of 'inflammable air' (hydrogen) and ordinary air contained in a glass vessel. One of those present noticed that the inside of the glass vessel was 'bedewed' with moisture, and Cavendish, having heard of the result, decided to follow it up. In one of his experiments he exploded a mixture containing measured volumes of hydrogen and air, and he found that 423 volumes of hydrogen combined with all the oxygen contained in 1000 volumes of ordinary air. Now he had previously found that ordinary air contained 21 per cent. of oxygen by volume, so that 1000 volumes of ordinary air would contain 210 volumes of oxygen. His result was, therefore, that 423 volumes of hydrogen combine with 210 of oxygen, and these numbers are almost exactly in the ratio of 2 to 1.

---

[1] Thus one of the characters in Boyle's *Sceptical Chymist* refers to the following 'obvious and easie analysis': 'For if you but consider a piece of green wood burning in a chimney, you will readily discern in the disbanded parts of it the four elements, of which we teach it and other mixt bodies to be composed. The fire discovers itself in the flame by its own light; the smoke by ascending to the top of the chimney, and there readily vanishing into air, like a river losing itself in the sea, sufficiently manifests to what element it belongs and gladly returnes. The water in its own form boiling and hissing at the ends of the burning wood betrays itself to more than one of our senses; and the ashes by their weight, their firiness, and their dryness, put it past doubt that they belong to the element of earth.'

Since the time of Cavendish many other scientists have made experiments with a view to finding the composition of water with the utmost possible exactness. The best work in this direction was carried out by E. W. Morley (1895), who worked with extraordinary patience and thoroughness, and as the average of many experiments, found that the volume of hydrogen combining with one of oxygen is 2·00269.

Questions

1. Hydrogen was passed over copper oxide, the weight of which became less by 7·93 gm. The water produced was absorbed in calcium chloride tubes, etc., and was found to weigh 8·92 gm. Find the percentage composition of water.

2. (i) When 49·75 gm. of copper oxide was reduced with hydrogen, the residue of copper was found to weigh 39·75 gm., and the water produced weighed 11·25 gm.

(ii) When 12 gm. of oxygen was exploded with 1·25 gm. of hydrogen, 11·25 gm. of water was produced, and 2 gm. of oxygen remained uncombined.

From (i), and also from (ii), find the composition of water by weight. What law is illustrated by your answers?

3. Draw labelled diagrams, one in each case, to show the preparation and collection of a small quantity of hydrogen, using (*a*) cold water, (*b*) steam. Describe any changes that may be observed. (Electrolytic methods will not be accepted.)

W.J. (*part*)

4. What is a reversible reaction? Give *three* examples of reactions of this type. Selecting *one* of these reactions, describe how you would show that it is reversible.

Under what conditions does a reversible reaction become balanced? *Oxf.*

5. Draw a labelled diagram of the apparatus you would use to demonstrate *either* (*a*) the synthesis of water from its elements, *or* (*b*) the decomposition of water by means of an electric current. Discuss the reactions involved.

How and under what conditions does water or steam react with sodium, calcium and magnesium? *Lond.*

6. Describe an experiment to determine the composition by volume of steam.

Show what information this experiment gives as to the atomicity of oxygen. *O.C.*

7. Explain what is meant by water of crystallisation.

What are the changes that are observed when crystals of copper sulphate are heated to a moderate temperature? How would you determine the percentage amount of water of crystallisation in these crystals?

If in your experiment the loss of water on heating the copper sulphate crystals was 36 per cent., how many molecules of water of crystallisation does this represent?

($H=1$; $O=16$; $S=32$; $Cu=63{\cdot}5$.) *W.J.*

8. You are supplied with a colourless, odourless liquid. How would you find out (*a*) whether it contains water, and if it does (*b*) whether it is pure water?

CHAPTER 10

HYDROGEN

In the last chapter we considered two methods by which hydrogen could be obtained. One method was by the electrolysis of water and the other was by the action of certain metals on water. Neither of these methods, however, is very convenient when we require to obtain a few jars quickly in the laboratory.

For convenience, we generally use the apparatus shown in fig. 10/1. A small handful of granulated zinc is placed in the flask, and dilute sulphuric (or hydrochloric) acid is poured down the thistle-funnel, the hydrogen being collected over water as shown. The equation is

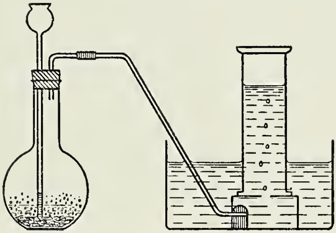


Fig. 10/1. Preparation of hydrogen

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

or

$$Zn + 2HCl = ZnCl_2 + H_2$$

(*N.B.* You will often have to *draw* an apparatus in which gas is being generated from the contents of a flask, usually liquid plus solid. Make sure (*a*) that the thistle funnel dips well below the liquid, and (*b*) that the exit tube does not reach much below the bottom of the cork.)

Prepared as above described, the gas has a rather unpleasant smell. This is partly due to the presence of traces of hydrogen sulphide, some of the sulphuric acid being 'reduced' by the zinc, especially as the acid becomes hot. We shall understand this better after reading Chapter 26 on Sulphuric Acid. Further, we always notice a quantity of 'dirt' floating about inside the flask. This is lead, a common impurity in ordinary zinc. It seems rather odd that lead should float, but in this case it is in a very finely divided form, something like dust.

Much purer hydrogen can be obtained by using magnesium instead of zinc ($Mg + H_2SO_4 = MgSO_4 + H_2$).

Unfortunately, however, an *ounce* of magnesium costs nearly as much as a *pound* of zinc.

The chief physical properties of hydrogen are as follows: It is without colour, taste or smell. It is practically insoluble in water. It is the lightest gas known, being only about 1/14th the weight of an equal volume of air. It is extremely difficult to liquefy—under ordinary pressure the liquid boils at $-252°$ C.

One of its chief chemical properties has already been mentioned—that when burnt it produces water. This may be shown by means of the apparatus sketched in fig. 10/2. The U-tubes contain calcium chloride to dry the gas—otherwise of course it might be argued that the water in the beaker was not produced by the burning of the hydrogen, but was previously present in the gas as water-vapour.

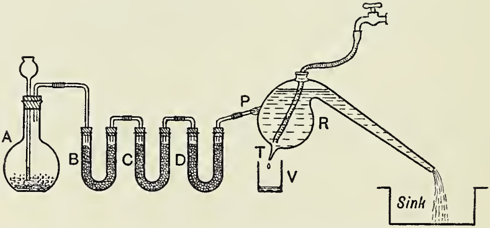


FIG. 10/2. Water produced by the burning of hydrogen

The yield of water is somewhat increased if the glass of the retort is drawn out into the projection T.

We can prove that the liquid *is* water by the tests described on p. 107.

Hydrogen forms a very explosive mixture with oxygen, or even with air. For this reason a light should *never* be applied to the exit-tube of a hydrogen generator until a sample of the gas has been tried and found to burn quietly. Neglect of this precaution has sometimes led to serious accidents.

Although a jet of hydrogen will not normally burn unless a light is applied, it will take fire if made to strike against a piece of very thin platinum wire (as in some types of gas-lighter), or a little platinised asbestos (p. 286). We have here an example of *catalysis*, a subject which is discussed on p. 288.

Hydrogen a Reducing Agent. Since hydrogen combines so readily with oxygen, forming water, it is worth while trying to find out what would happen if we passed hydrogen over the various oxides which we prepared by burning different elements in oxygen. The apparatus is shown in fig. 10/3.

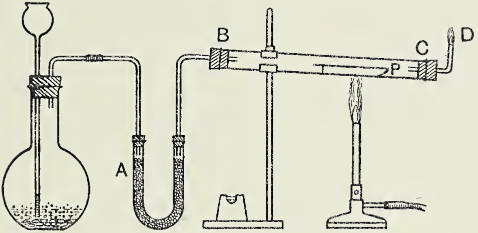


FIG. 10/3. Passing hydrogen over a heated oxide

The hydrogen is passed through a calcium chloride tube, A, to dry it, and then passes through a hard-glass combustion tube, BC, in which is a porcelain boat, P, containing the oxide. The escaping hydrogen may be lighted at D, care being taken first to make sure that a sample of it burns quietly.

It is found that

(i) Unless the oxide is heated there is no change whatever.

(ii) Even when heat is applied, some oxides (e.g. those of magnesium and calcium) are not changed. In other cases, however, the oxide is changed into the metal, and a liquid which proves to be water makes its appearance near the end, C, of the combustion tube.

This result is not surprising. No doubt the hydrogen has taken oxygen from the oxide, and combining with it, has formed water. In the case of copper oxide, the equation would be

$$CuO + H_2 = Cu + H_2O$$

When a substance loses oxygen in this way it is said to be ***reduced,*** while the substance which gains the oxygen is said to be ***oxidised.*** In this case, for instance, we should say that the copper oxide has been reduced to copper, while the hydrogen has been oxidised to water. A substance which brings about reduction is called a ***reducing agent,*** while one which brings about oxidation is called an ***oxidising agent.*** Here, hydrogen is the reducing agent and copper oxide is the oxidising agent.

In Chapter 25, however, we shall see that the term 'reduction' now has a wider meaning than that just given.

It is interesting to notice that Priestley carried out a number of experiments which in principle were very similar to the one just described. In one of them he used an oxide of lead ('red lead' or 'minium'), and placed it in a bell-jar containing 'inflammable air' (as he called hydrogen) which had been collected over water. He now heated the red lead by means of the burning-glass already mentioned.

> 'As soon as the minium was dry by means of the heat thrown upon it,' he says, 'I observed that it became black, and then ran into the form of perfect lead; at the same time that the air[1] diminished at a great rate, the water ascending within the receiver. I viewed this process with the most eager and pleasing expectation of the result. . . . Seeing the metal to be actually revived, and that in a considerable quantity, at the same time that the air[1] was diminished, I could not doubt but that the calx was actually imbibing something from the air;[1] and from its effects in making the calx into metal, it could be no other than that to which chemists had unanimously given the name of phlogiston.'

[1] i.e. the 'inflammable air' (hydrogen).

We can see how Priestley explained the result. Red lead or minium, he argued, is the 'calx' formed when lead loses its phlogiston through being heated in the air. Let the calx 'imbibe' phlogiston again and, of course, you get the lead!

Nascent Hydrogen. In Chapter 37 we shall meet with a brown substance called ferric chloride, $FeCl_3$, and a green one, ferrous chloride, $FeCl_2$ (at least, they have these colours in solution). Now, if to the brown solution of ferric chloride we add a little zinc and hydrochloric acid, the colour gradually changes to green. As this is the colour of ferrous chloride ($FeCl_2$) it seems reasonable to express the change thus:—

$$[FeCl_3 + H = HCl + FeCl_2]$$

$$2FeCl_3 + H_2 = 2HCl + 2FeCl_2$$

(the hydrogen having been produced, of course, by the action of the acid on the zinc).

In this experiment the hydrogen was generated *in contact with the ferric chloride*. Now let us carry out a second experiment in which the hydrogen is generated *in a separate flask*, and *then* passed into the brown solution of ferric chloride. This time there is no change in colour, no matter how long we allow hydrogen to pass through the liquid. How are we to account for the difference?

We saw in Chapter 4 that the hydrogen molecule consists of a pair of atoms—we represent it as H_2. Now it is not reasonable to suppose that the atoms were *always* joined together. When just liberated from hydrochloric acid they would exist, at least for an instant, as single atoms. These single atoms seem to possess great chemical activity, and in ordinary circumstances combine with one another ($H + H = H_2$). If, however, at the moment they are produced they find themselves in contact with some other substance with which they can react (in this case ferric chloride), reaction takes place. If this theory is correct (it is not accepted by everybody), our equation should read

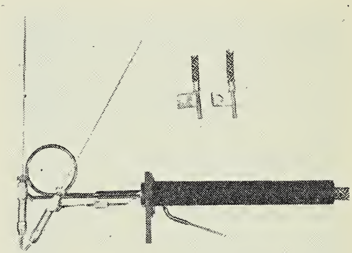
$$FeCl_3 + H = HCl + FeCl_2$$

and *not*

$$2FeCl_3 + H_2 = 2HCl + 2FeCl_2$$

because single atoms and not pairs of atoms are concerned in the change. This very active form of hydrogen whose molecules consist of single atoms is said to be *nascent* (Lat. *nascor* = I am born). It is hydrogen at the moment of its birth, so to speak.

Since atoms of hydrogen combine so easily with one another, we should expect to find that they are difficult to separate, and this is in general the case. However, Dr. Irving Langmuir, of the General Electric Company, showed in 1912 that if hydrogen passes through an electric arc formed between tungsten electrodes, it becomes largely monatomic (i.e. its molecules then consist of single atoms). In the illustration the arc is formed at the point of the V, and the monatomic hydrogen is blown forward by the stream of ordinary hydrogen from behind. Just beyond the arc the single atoms recombine with so much energy as to produce a very high temperature indeed—high enough to melt tungsten for instance (m.p. 3400° C.). The 'atomic hydrogen torch,' as it is called, has many uses. In the illustration (p. 118) it is being employed for welding pipeline in one of the south-western states of America.



Atomic hydrogen torch

By courtesy of International Gen. Elec. Co., New York

Uses. At the beginning of this century hydrogen was regarded as a rather useless element. It was (and is) a constituent of valuable fuels such as coal-gas and water-gas (p. 186), but taken by itself it had scarcely any uses except for filling balloons, etc., and for contributing to the oxy-hydrogen flame (a flame of hydrogen fed with oxygen. It is very hot, and when it strikes upon a cylinder of quicklime the latter gives out a brilliant white light known as the limelight).

Nowadays, however, hydrogen is used in enormous quantities for the manufacture of synthetic ammonia (Chapter 28). Much smaller quantities are used in the treatment of oils and soft fats, and in the manufacture of a sort of artificial petrol.

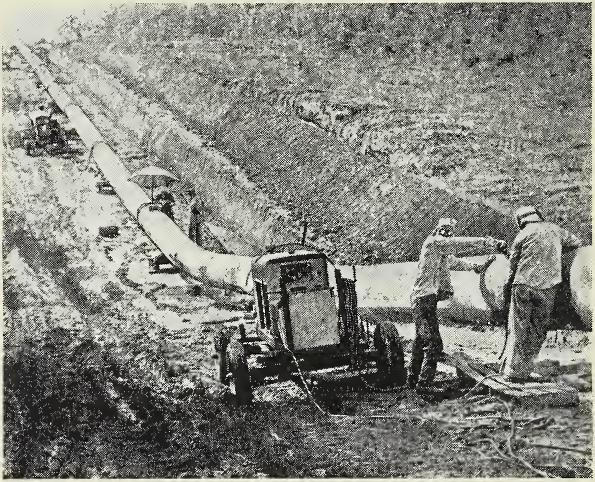
Synthetic ammonia is discussed in Chapter 28, fats and oils in the Introduction; but we must say something about the manufacture of petrol from coal and hydrogen.

Coal is a very complex substance, containing a high percentage of carbon and much smaller percentages of hydrogen and oxygen. There are small quantities of other elements (chiefly nitrogen and sulphur), but we can ignore these for our present purpose.

Petrol has hitherto been obtained from a crude natural oil, which is a mixture of many hydrocarbons (i.e. compounds of carbon and hydrogen), and taking these altogether, the amount of hydrogen present, for a given amount of carbon, is roughly twice as great as in coal.

With these facts in mind, a German chemist named Bergius thought that, if he heated coal with hydrogen under suitable conditions, he might obtain a mixture of hydrocarbons closely resembling crude oil. The quantity of hydrogen would have to be sufficient (i) to combine with the unwanted oxygen of the coal, forming steam, which could easily be removed, and (ii) to provide the higher proportion of hydrogen which distinguishes the 'crude oil' hydrocarbons from coal. After many trials he found out the best conditions. The coal is ground up finely enough to pass through a mesh of 2 mm. It is then worked into a paste with some cheap oil, and heated to about 450° C. in contact with hydrogen at a high pressure (200 atmospheres). The mixture of hydrocarbons obtained can be separated (by 'fractional distillation') into petrol, fuel oil, diesel oil and lubricating oil. The process was operated on a very considerable scale during the war, and also at the I.C.I. works at Billingham in this country, which was capable of turning out 45 million gallons per year of motor and aviation spirit. During and since the war, creosote has been used as raw material at Billingham to the exclusion of coal, the post-war cost of which in this country is too high for an economic process. Hydrogenation of brown coal in Eastern Germany has, however, continued.

Industrial Methods of Preparation. It will be obvious that for such purposes as those just mentioned the amount of hydrogen required must be very great—it is certainly well over 100,000 tons per year. Most of it is manufactured by what is known as the Bosch process. Here we start with water-gas, a mixture of carbon monoxide and hydrogen obtained by passing steam over heated coke ($H_2O + C = H_2 + CO$). The water-gas is mixed with steam, and passed over a suitable catalyst (iron) at a temperature of 400°–500° C. In these circumstances the monoxide in the water-gas is converted into dioxide ($CO + H_2O = CO_2 + H_2$), and the latter is removed by solution in cold water under pressure.



By courtesy of International General Electric Co., New York

Welding pipeline by means of the atomic hydrogen torch

The hydrogen employed in making hard fats from fish oils and soft fats (*Introduction*, p. 4), for use in the soap and margarine industries, is largely obtained by the reversible steam–iron reaction already discussed on pp. 97–99. The iron oxide formed, Fe_3O_4, is reduced to iron by means of water-gas, after which the iron is made to react with a further quantity of steam, and so on.

In smaller factories this 'fat hardening' process is carried out by means of hydrogen obtained from the electrolysis of water. Oxygen, of course, is produced at the same time, and in some districts this finds a ready sale for use in the oxy-acetylene welding process.

Questions

N.B. *See note in italics*, p. 68.

1. Describe carefully how you would prepare a few gas jars of hydrogen from sulphuric acid and zinc. Draw a diagram of the apparatus you would use. *Camb.*

2. Calculate the percentage of water of crystallisation in zinc sulphate, $ZnSO_4.7H_2O$.

3. By the action of dilute sulphuric acid on magnesium, crystals having the following percentage composition may be obtained: magnesium, 9·8; sulphur, 13·0; oxygen, 26·0; water of crystallisation, 51·2. Find the simplest formula of the substance.

4. Sketch and label, *without* further description, an apparatus for preparing dry hydrogen and burning it at a jet fixed under a flask cooled by running water.

What substance would you observe to be formed on the flask? Describe *three* tests by which you would prove its identity. *Oxf.*

5. 'Hydrogen is a reducing agent.' Explain the meaning of this statement, and describe briefly (with a sketch of the apparatus used) how you would prove it.

6. When hydrogen is passed through a solution of ferric chloride there is no change of colour.

When hydrochloric acid is added to such a solution, and then zinc (to produce hydrogen), the colour gradually changes from yellowish brown to a watery green.

How do you account for these different results?

7. How is hydrogen prepared on a manufacturing scale?

8. State, and explain briefly, three industrial uses of hydrogen. *Camb.* (*part*)

CHAPTER 11

GAY-LUSSAC'S LAW AND AVOGADRO'S HYPOTHESIS

In the year 1804 a great scientist and explorer named Humboldt had just completed an adventurous journey in which he had paid special attention to South America. Among many questions he had set out to answer was one with reference to air—whether air varies in composition according to the part of the world in which it is found. Accordingly he brought a great many samples home, and got a French chemist named Joseph Louis Gay-Lussac to help him analyse them.

Their method was to mix a quantity of hydrogen with the air and then explode the mixture by means of an electric spark. This caused the total volume to contract, and by observing the amount of contraction, the volume of oxygen present in the air could easily be found. 5 c.c. of oxygen, for instance, would combine with 10 c.c. of hydrogen, producing water, the volume of which would be quite negligible. Thus the total volume of gas present would diminish by 15 c.c., and one-third of this would represent the required volume of oxygen (cf. Ex. 5 on p. 131). Evidently the working out depends on a knowledge of the proportions in which hydrogen and oxygen combine (2 : 1). Gay-Lussac might have used Cavendish's result for this, but he decided to obtain one of his own, and as the mean of many experiments he found that 100 c.c. of oxygen combine with 199·89 of hydrogen. (The most recent experiments give the ratio 100 : 200·24, and considering the apparatus Gay-Lussac used, we must consider his answer a remarkably good one.)

He was much impressed with the fact that the two gases combined in what is practically the simple ratio by volume of 2 : 1. When he had finished analysing all Humboldt's air samples[1] his mind turned again to this 'simple ratio' question, and he wondered whether other gases also combined in a simple ratio by volume. These are some of the results he obtained:

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[1] And many of his own. He was particularly anxious to find out (among other things) whether the composition of the air varies at

1 vol. of hydrogen combines with 1 vol. of chlorine, giving 2 vols. of hydrogen chloride.

2 vols. of carbon monoxide combine with 1 vol. of oxygen, giving 2 vols. of carbon dioxide.

1 vol. of nitrogen combines with 3 vols. of hydrogen, giving 2 vols. of ammonia.

Let us consider these results for a moment. We notice first the volume of the product is not always equal to the sum of the volumes of the gases that have gone to make it. It *may* be, as in the case of hydrogen chloride. But there is more often a contraction, e.g. 1 vol. of nitrogen and 3 of hydrogen give only 2 vols. of ammonia, not 4.

The main point, however, is that of the *simple ratio.* Supposing you were doing the carbon monoxide experiment, for instance, and you found that to combine with 24 c.c. of carbon monoxide you required exactly 12 c.c. of oxygen, and that the carbon dioxide produced had a volume of 24 c.c., you would be struck with the simple ratio between the numbers 24, 12, 24; and so was Gay-Lussac. He summed up his results in what is known as the ***Law of Gaseous Volumes*** (1808), which may be stated thus: *When two gases combine, they do so in volumes which bear a simple ratio to one another, and to the volume of the product if the latter be a gas.*

Naturally Gay-Lussac and other chemists began to do some hard thinking over the question, '*Why* should gases react in such simple ratios by volume?' They argued something like this (remember that Dalton had published his Atomic Theory only a few months before):

(i) When hydrogen and chlorine combine, each *atom* of hydrogen combines with an *atom* of chlorine.

(ii) But experiment shows that 1 *volume* of hydrogen combines with 1 *volume* of chlorine.

(iii) Therefore 1 volume of hydrogen must contain as many atoms as 1 volume of chlorine.

---

great altitudes, so he decided to obtain samples. He borrowed a crazy balloon that Napoleon had used in his Egyptian campaign, and as nobody would risk the danger of an ascent, he went up himself (September 1804). He attained a height of 23,000 feet, obtained his samples, and then went quietly on with his analysis.

Similar arguments, of course, would apply to other cases, and so the conclusion drawn was that 'Equal volumes of all gases, under the same conditions of temperature and pressure, contain equal numbers of atoms.' We will call this 'Berzelius' Hypothesis,' because it was specially advocated by the Swedish chemist Berzelius, though other prominent chemists held much the same ideas.

N.B. In those early days scientists used the word atom with reference not only to an element, but to a compound—they would speak of an atom of hydrogen chloride, for instance, where we should now say 'molecule.' To avoid confusion, however, they sometimes used the term 'compound atom' in such cases.

Trouble arose almost at once—it arose over that very case of hydrogen chloride. Let us see how it works out.

By experiment

1 vol. hydrogen combines with 1 vol. chlorine, forming 2 vols. hydrogen chloride.

Let 1 vol. of hydrogen contain x atoms.

$\therefore$ by Berzelius' Hypothesis

1 vol. of chlorine must contain x atoms, and

2 vols. of hydrogen chloride must contain $2x$ (compound) atoms.

$\therefore$ (going back to the experimental result)

x atoms hydrogen and x atoms chlorine give $2x$ atoms hydrogen chloride.

Divide through by x.

$\therefore$ 1 atom hydrogen and 1 atom chlorine give 2 atoms hydrogen chloride.

Now think of these two 'atoms' of hydrogen chloride—two separate portions. *Each* of them contains hydrogen. Therefore our original '1 atom of hydrogen' must have broken into two halves! (And the same, of course, for the chlorine.)

But it is one of the main points of Dalton's theory that an atom is the *smallest* portion and *cannot* be broken. It is not very surprising therefore that Dalton protested against the conclusion. He suggested that Gay-Lussac's experimental results were probably wrong, in which case there would be no foundation for Berzelius' Hypothesis, which was based on them.

Yet many scientists—and in particular an Italian physicist named Avogadro—were unwilling to reject the hypothesis altogether. They brought forward a strong additional argument. 'All gases behave in the same way when heated (Charles' Law) and when compressed (Boyle's Law),' they said, 'and therefore all gases must be built up in much the same way. What more likely than that they should all (for equal volumes) contain equal numbers of atoms?'

And very soon Avogadro saw a way through the difficulty—the difficulty of an atom breaking up into two parts. 'Of course you cannot break an atom,' he said in effect, 'but suppose the atoms are combined *in pairs*; then a *pair* of atoms might easily break up into two separate portions.'

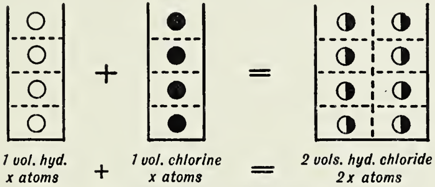

FIG. 11/1. Equal volumes contain equal numbers of *atoms* (simple or compound)

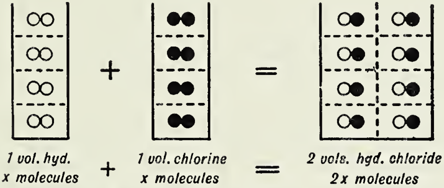

FIG. 11/2. Equal volumes contain equal numbers of *molecules*

When Dalton (and others) thought of a jar of hydrogen, they imagined a large number of single, separate atoms, like a lot of extremely tiny billiard balls. Avogadro began to think of hydrogen in another way—he thought of the 'billiard balls' stuck together in pairs, and called them molecules. Accepting the first view, Gay-Lussac's results lead to the awkward conclusion that *atoms* must have broken into halves (fig. 11/1), but Avogadro's view leads to the much easier conclusion that *molecules* have broken into halves (fig. 11/2).

Avogadro's suggestion clears up the whole situation so completely that one would have expected it to be accepted at once. Actually it did not win acceptance for nearly forty years. It was put forward in 1811, and after some controversy it seems to have been forgotten altogether. However, in 1858 another Italian named Cannizzaro showed how clearly it accounted for a large number of experimental facts, and since then it has been universally accepted. Avogadro had died in 1856, so he never received much credit for his 'hypothesis,' as his theory is usually called. It may be stated as follows: *Equal volumes of all gases, under the same conditions of temperature and pressure, contain equal numbers of molecules.* We shall often have occasion to make use of it.

Fig. 11/2 implies that the molecule of hydrogen contains only 2 atoms, but it could equally well 'break into halves' if it contained 4, 6, 8 . . . There is independent evidence, however, that the number of atoms is only 2. The same applies to the molecule of chlorine, and of oxygen (cf. p. 104, where it was shown that 1 molecule of steam contains half a molecule of oxygen, which half molecule must therefore consist of at least 1 atom).

It is convenient here to mention the term ***atomicity,*** which means *the number of atoms contained in* 1 *molecule of an element.* Thus the atomicity of hydrogen, chlorine and oxygen is in each case 2, and we write H_2, Cl_2, O_2. The molecules of mercury *vapour* consist of single atoms, i.e. mercury vapour has an atomicity of 1. Ozone (Chapter 14) has an atomicity of 3, and phosphorus *vapour* of 4, so we write O_3 for the first and P_4 for the second.

We do not know the atomicity of elements in the solid condition. We write C, Mg, Al, etc., for simplicity, without implying that the atomicity is 1.

The Molecules of a Gas. In thinking out problems about gases, we often find it helpful to have some rough idea of what the molecules are like and what they are doing. First of all, then, the molecules are almost incredibly small. One cubic centimetre of any gas at N.T.P. contains about 271×10^{17} of them—271 and 17 noughts in less than a thimbleful of gas! Somebody has calculated that this number 271×10^{17} is about equal to the number of grains of sand that would be present in a cubical box full of sand and measuring a mile each way.

Yet in a gas the molecules are not tightly packed together—the average distance between one and another is very much greater than the diameter of the molecule itself. Further, the molecules are in rapid movement, shooting about with a speed which is sometimes greater, sometimes less, but which on an average is about equal to that of a rifle bullet. Collisions and rebounds must be frequent in the extreme.

Molecules and Pressure. The constant pounding of the molecules against the walls of the containing vessel is what causes *pressure*. If the gas (say by the action of a piston) is compelled to occupy a smaller volume, the molecules will strike one or other of the containing walls more frequently because they have not so far to go. This causes an increase of pressure—in fact, the smaller the volume, the greater the pressure, as Boyle's Law tells us.

If, on the other hand, we apply heat to the vessel containing the molecules, the latter begin to move with greater speed and strike the walls with increased force, once more producing greater pressure. If you heated a corked flask containing only air, this increased pressure would probably cause the cork to be blown out.

The student sometimes finds it hard to understand how Avogadro's Hypothesis can be true, because a molecule of carbon dioxide for instance, CO_2, must surely take up more room than one of carbon monoxide, CO. No doubt it does, and if the molecules were tightly packed together it would not be possible to get so many of the CO_2 molecules into a given space. As it is, all that happens is that the average distance between the carbon dioxide molecules is just a little less than between those of carbon monoxide, and a given volume contains equal numbers of each. If a committee arranging a whist drive find that they have tables, etc., to accommodate a hundred people, they do not trouble whether the people to whom they sell the tickets are fat or thin.

Some Consequences of Avogadro's Hypothesis. The two statements proved below should be carefully remembered.

(1) *If* m *is the molecular weight of a gas and* d *is its density relative to hydrogen, then* $m=2d$.

Density relative to hydrogen $=d$,
i.e. a certain volume of the gas weighs d times as much as an equal volume of hydrogen.

$\therefore$ x molecules of the gas weigh d times as much as x molecules of hydrogen. (For the number of molecules in 'a certain volume' of each will be the same. AVOGADRO)

$\therefore$ 1 mol. of the gas weighs d times as much as 1 mol. of hydrogen, i.e. d times as much as 2 *atoms* of hydrogen.

$\therefore$ 1 mol. of the gas weighs $2d$ times as much as 1 atom of hydrogen, i.e. its molecular weight is $2d$.

(2) *The gram-molecule of any gas occupies* 22·4 *litres at N.T.P.*

(*N.B.* The gram-molecule of a substance is the number of grams that corresponds to its molecular weight. Thus molecular weight of carbon dioxide, CO_2, is $12+32=44$, and so 44 gm. would be a gram-molecule of carbon dioxide; or we may say that 44 gm. is its *gram-molecular weight* (*G.M.W.*).

The gram-molecule of hydrogen, H_2, would be 2 gm., and it will be assumed as an experimental result that this quantity occupies 22·4 litres at N.T.P.)

Let the molecular weight of any gas $=m$.

$\therefore$ the gram-molecule $=m$ gm.

Also the density relative to hydrogen $=\frac{1}{2}m$ (proved above).

$\therefore$ $\frac{1}{2}m$ gm. of the gas occupies the same volume as 1 gm. of hydrogen.[1]

$\therefore$ m gm. occupies same volume as 2 gm. of hydrogen, i.e. the gram-molecule occupies 22·4 litres; or we may say that the *gram-molecular volume* (*G.M.V.*) of any gas is 22·4 litres.

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[1] If this is not clear, compare: Density of mercury relative to water $=13·6$.
$\therefore$ 13·6 gm. of mercury occupies the same volume as 1 gm. of water.

How Vapour Density is Determined. Since the molecular weight of a compound is equal to twice its vapour density, it is important to be able to determine the latter quantity.

Very likely you have found for yourself, roughly, the density of a gas such as carbon dioxide. You weigh a dry flask, fill it with dry carbon dioxide by displacing air upwards, and weigh again. You then find the volume of the flask with a measuring jar, read the temperature and pressure, and work out your result as in the following example:

Wt. of flask + air	109·74 gm.
,, ,, + carbon dioxide	110·01 ,,

Vol. of flask, 420 c.c. Temp., 14° C. Pressure, 75·2 cm.

We shall assume that wt. of 1 litre of air at N.T.P. = 1·29 gm.

The wt. of a litre of air, or of carbon dioxide, depends on temp. and pressure; and it is easily shown that this is true for the *difference* between these weights.

Now at 14° C. and 75·2 cm. pressure, 420 c.c. carbon dioxide weighs 110·01 – 109·74 = 0·27 gm. *more* than 420 c.c. air.

$\therefore$ at N.T.P. this excess $= 0{\cdot}27 \times \frac{287}{273} \times \frac{76}{75{\cdot}2} = 0{\cdot}29$ gm.

$\therefore$ excess for 1000 c.c. $= 0{\cdot}29 \times 1000/420 = 0{\cdot}69$ gm.

$\therefore$ wt. of 1 *l.* of carbon dioxide at
N.T.P. $= 1{\cdot}29 + 0{\cdot}69 = 1{\cdot}98$ gm.

$\therefore$ density of carbon dioxide rel. to hydrogen $= 1{\cdot}98 \div 0{\cdot}09 = 22{\cdot}0$.

$\therefore$ mol. wt. $= 22{\cdot}0 \times 2 =$ ***44·0.***

In the case of a liquid which can be vaporised without decomposition, the vapour density may be found by 'Victor Meyer's method.' Suppose, for instance, we wish to find the vapour density of carbon disulphide (b.p. 46° C.).

The apparatus is as shown in fig. 11/3. Water is boiled in the jacket, A, causing air in the inner tube, BC, to expand, so that bubbles escape at D. Soon the air in BC reaches a steady average temperature, and bubbles cease to escape.

Meanwhile a small quantity (say 0·1 gm.) of carbon disulphide has been accurately weighed in a tube about 3 cm. long. This is shaped like a test-tube, but is narrow enough to drop down BC. It is closed at one end with a cork.

The air in BC having reached the steady state (i.e. no bubbles escaping), the cork at B is removed and the little tube is dropped in. The cork is at once replaced.

The carbon disulphide quickly vaporises, and the pressure easily blows off the cork of the little tube. The vapour then displaces an equal volume of air, which is collected and measured in the graduated tube E.

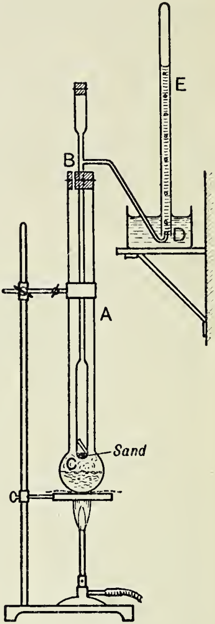

FIG. 11/3
Vapour density by Victor Meyer's method

Let us suppose that after reduction to N.T.P. the volume of air=33·3 c.c., and that the weight of carbon disulphide=0·114 gm.

In the process of vaporising, the carbon disulphide has not changed in *weight.*

∴ 33·3 c.c. of vapour at N.T.P. weighs 0·114 gm.

∴ 1000 c.c. weighs

$$\frac{0{\cdot}114}{33{\cdot}3} \times 1000 = 3{\cdot}42 \text{ gm.}$$

But 1000 c.c. of hydrogen at N.T.P. weighs 0·09 gm.

∴ density relative to hydrogen $=3{\cdot}42 \div 0{\cdot}09 = 38{\cdot}0$, and mol. wt. $=38{\cdot}0 \times 2 = \mathbf{76{\cdot}0}$.

Atomic Weights from Vapour Densities. We have now considered methods for finding the vapour densities both of gases and of the vapours of volatile liquids.

Now if an element forms a number of compounds which are either gases or volatile liquids—and many elements do—we can find its atomic weight. We will illustrate the method using carbon as an example. Column (1) of the table gives a number of such compounds, and Column (2) their vapour densities. From $m=2d$ we readily obtain Column (3).

Substance	*Vapour density* (d)	*Mol. wt.* (m)	*Wt. of carbon in* m *gm.*
Carbon dioxide	22	44	12
Benzene	39	78	72
Chloroform	59·7	119·4	12
Acetylene	13	26	24
Ether	37	74	48
Methane	8	16	12
Alcohol	23	46	24
Pentane	36	72	60

It is important to notice that *Column* (4) *is quite independent of* (2) *and* (3). Each result in Column (4) is obtained as the result of an analysis, and the methods used are for the most part rather beyond us at present (though one that works for carbon dioxide will be described on pp. 163–4). Thus from his analysis the chemist would find, for example, that the percentage of carbon in pentane is 83·3, and therefore the weight of carbon in 72 gm. (m) is $\frac{83 \cdot 3}{100} \times 72 = 60 \cdot 0$.

This last column, then, gives the weight of all the carbon atoms in the molecule. It is more, or less, according as the molecule contains more or less carbon atoms. The smallest number we notice is 12. It looks as though in these cases (carbon dioxide, chloroform, and methane) we have the smallest possible number of carbon atoms in the molecule, i.e. 1. Many other volatile compounds of carbon have been examined, and we find that the smallest weight of carbon ever found in m gm. of the compound is 12; so we infer that 12 is really the atomic weight.

We shall conclude this chapter by working out a number of typical calculations.

N.B. In calculations on the volumes of gases we usually assume that at N.T.P. 1 litre of hydrogen weighs 0·09 gm., or alternatively that 2 gm. of hydrogen (the gram-molecule) occupies 22·4 litres.

Unfortunately these numbers are not quite consistent. For if 0·09 gm. is the weight of 1 litre, then 2 gm. is the weight of $1 \div 0 \cdot 09 = 22$ litres.

Between 22·2 and 22·4 there is a discrepancy of nearly 1 per cent. This arises from the fact that the unit of atomic weight is not, strictly speaking, the weight of an atom of hydrogen, but one-sixteenth of the weight of an atom of oxygen, i.e. the atomic weight of oxygen is taken as 16·00, and on this scale we have $H = 1 \cdot 008$. The gram-molecule of hydrogen is then 2·016 gm., and at N.T.P. this weight of gas *has* a volume of 22·4 litres.

In calculations it is usual to assume that $H = 1$, unless there is a statement to the contrary.

Example 1. *Arrange the following gases in order of density, and state which are heavier and which lighter than air: hydrogen chloride, ammonia, chlorine, methane, oxygen (at N.T.P. 1 l. of hydrogen weighs* 0·09 *gm. and* 1 *l. of air* 1·29 *gm.)*

Hydrogen chloride, HCl, has a mol. wt. of $1 + 35 \cdot 5 = 36 \cdot 5$.

$\therefore$ its density relative to hydrogen $= \frac{1}{2} \times 36 \cdot 5 = 18 \cdot 25$.

$\therefore$ 1 litre of the gas weighs $18 \cdot 25 \times 0 \cdot 09 = 1 \cdot 64$ gm.

In a similar way we find that—

1 litre of ammonia, NH_3, weighs $\frac{1}{2}(14+3)\times 0{\cdot}09=0{\cdot}765$ gm.
1 litre of chlorine, Cl_2, weighs $\frac{1}{2}(35{\cdot}5+35{\cdot}5)\times 0{\cdot}09=3{\cdot}19$ gm.
1 litre of methane, CH_4, weighs $\frac{1}{2}(12+4)\times 0{\cdot}09=0{\cdot}72$ gm.
1 litre of oxygen, O_2, weighs $\frac{1}{2}(16+16)\times 0{\cdot}09=1{\cdot}44$ gm.

The order of densities is chlorine, hydrogen chloride, oxygen, ammonia, methane. The first three weigh more than 1·29 gm. per litre, and are therefore heavier than air, while ammonia and methane are lighter.

N.B. Mistakes are often made in connection with chlorine, oxygen, nitrogen and hydrogen. The molecule in each of these cases contains *two* atoms (Cl_2, O_2, N_2, H_2). Thus the *molecular* weight is twice the *atomic* weight. Note particularly that at N.T.P., 22·4 litres = *two* grams (not one) of hydrogen.

Example 2. *What would be the composition by volume of* (i) *ammonia,* (ii) *steam, and* (iii) *nitric oxide?*

Ammonia. Write the equation representing its decomposition

$$[NH_3=N+3H] \qquad 2NH_3=N_2+3H_2$$

Thus from 2 *molecules* of ammonia we obtain 1 *molecule* of nitrogen and 3 *molecules* of hydrogen.

But it follows from Avogadro's Hypothesis that the volumes of different gases are proportional to the number of molecules.

∴ from 2 *volumes* of ammonia we obtain 1 *volume* of nitrogen and 3 *volumes* of hydrogen.

Thus ammonia consists of half its volume of nitrogen combined with one and a half times its volume of hydrogen.

Steam. $[H_2O=H_2+O] \qquad 2H_2O=2H_2+O_2$
Working as before, we see that steam consists of its own volume of hydrogen combined with half its volume of oxygen.

Nitric Oxide. $[NO=N+O] \qquad 2NO=N_2+O_2$
The equation shows that nitric oxide consists of half its volume of nitrogen combined with half its volume of oxygen.

N.B. In answering such questions it is essential that the equation should indicate *complete molecules.*

Example 3. *A certain gaseous hydrocarbon contains* 92·3 *per cent. of carbon, and* 1 *litre of it at N.T.P. weighs* 1·17 *gm. Find its formula.*

We obtain the simplest formula by the method explained on pp. 49–50. Thus we have (top of next page)—

Elements	*Percentage*	*These numbers are proportional to*	*If* 1 = H
Carbon	92·3	$92{\cdot}3\times\frac{12}{92{\cdot}3}=12$	12 = C
Hydrogen	7·7	$7{\cdot}7\times\frac{12}{92{\cdot}3}=\ 1$	1 = H

Thus the *simplest* formula is CH.

Now its density relative to hydrogen is $\frac{1{\cdot}17}{0{\cdot}09}=13$.

$\therefore$ molecular weight $=13\times 2=26$.

If the formula were CH, the molecular weight would be $12+1=13$; but it is 26.

$\therefore$ the formula must be $\boldsymbol{C_2H_2}$.

N.B. C_2H_2 would be called the *molecular formula,* in contrast with the *simplest,* or *empirical, formula* CH.

Example 4. *What volume of sulphur dioxide measured* (a) *at* 0° *and* 760 *mm. pressure,* (b) *at* 13° *and* 722 *mm. pressure, would be formed by the combustion of* 8 *gm. of sulphur?*

The equation is

$$\begin{array}{l} S+O_2 \quad =S \quad O_2 \\ 32 \quad 16\times 2=32+32. \end{array}$$

Evidently by the oxidation of 32 gm. of sulphur we obtain 1 gram-molecule of sulphur dioxide, i.e. 22·4 litres at N.T.P.

$\therefore$ by oxidation of 8 gm. we obtain $\frac{22{\cdot}4}{32}\times 8=$ ***5·6 litres.***

At 13° C. and 722 mm. the volume would be

$$5{\cdot}6\times\frac{286}{273}\times\frac{760}{722}=\boldsymbol{6{\cdot}18\ litres.}$$

Example 5. 50 *c.c. of a mixture of nitrogen and oxygen were added to* 20 *c.c. hydrogen and the mixture sparked. After reaction,* 46 *c.c. of gas were left, and were found to consist of nitrogen and hydrogen only. Assuming that all volumes are measured at the same room temperature and pressure, calculate the percentage of oxygen in the original mixture of gases. W.J.*

The reaction is between hydrogen and oxygen only, the nitrogen taking no part.

From the equation $2H_2+O_2=2H_2O$ we learn that 2 c.c. of hydrogen combine with 1 c.c. of oxygen, and *the* 3 *c.c. of gas* *practically disappear altogether*, because at room temperature the water would not appear as a gas.

Thus for a contraction of 3 c.c. the volume of oxygen present was 1 c.c.

In the case before us the contraction is $(70-46)=24$ c.c.

∴ the volume of oxygen was $\frac{1}{3}$ of $24=8$ c.c.

This was present in 50 c.c. of the mixture.

∴ percentage of oxygen was ***16***.

Example 6. *A mixture of* 6 *c.c. of hydrogen,* 3 *c.c. of carbon monoxide, and* 10·5 *c.c. of oxygen was introduced into a eudiometer over mercury and exploded by an electric spark. What is the composition by volume of the product of the reaction, all the measurements being made at the same temperature and pressure, the former being above* 100° *C.? Camb.*

The hydrogen and carbon monoxide would each be oxidised thus:

$$\text{(i)}\ 2H_2 + O_2 = 2H_2O;$$
$$\text{(ii)}\ 2CO + O_2 = 2CO_2.$$

Equation (i) tells us that 6 c.c. of hydrogen would combine with 3 c.c. of oxygen, and that 6 c.c. of steam would be produced (the temperature is above 100° C.).

Equation (ii) tells us that 3 c.c. of carbon monoxide would combine with 1·5 c.c. of oxygen, and that 3 c.c. of carbon dioxide would be produced.

Thus in all, $3+1{\cdot}5$, or 4·5 c.c. of oxygen would be used up, leaving $10{\cdot}5-4{\cdot}5=6$ c.c.

Therefore the final product consists of ***oxygen 6 c.c. (40 per cent.), steam 6 c.c. (40 per cent.), and carbon dioxide 3 c.c. (20 per cent.).***

Questions

N.B. *In all further calculations in this book, unless alternative information is given in the question, it is to be assumed that* (i) *atomic weights are as given in the 'approximate' column in the table (end of book), and* (ii) *the gram-molecule of a gas occupies* 22·4 *litres at N.T.P.*

A

1. 37 c.c. of oxygen was added to 14 c.c. of carbon monoxide and the mixture was exploded. The product measured 44 c.c. of which 30 c.c. consisted of unused oxygen, the rest being carbon dioxide. Show that we have here an example of Gay-Lussac's Law.

2. A mixture of 12 c.c. methane and 53 c.c. oxygen was exploded. The volume of the product was 41 c.c., and of this 29 c.c. consisted of excess of oxygen, the rest being carbon dioxide. Show that these numbers illustrate Gay-Lussac's Law.

3. From the equation $Zn + H_2SO_4 = ZnSO_4 + H_2$, calculate the volume of hydrogen obtained from 13·08 gm. of zinc.
(Zn = 65·4.) *O.C. (part)*

4. Define the molecular weight of a gas.

In an experiment to find the molecular weight of a gas the following weighings were made. Complete the calculation.

Weight of evacuated flask = 36·550 gm.
Weight of flask filled at N.T.P. with hydrogen = 36·950 gm.
Weight of flask filled at N.T.P. with given gas = 39·950 gm.
J.M.B.Alt. (part)

5. Find the empirical formula of a compound which contains C, 92·3; H, 7·7.

Its vapour density is 39. What is its molecular weight?
O.C. (part)

6. Calculate the weight of sulphur in 11·2 litres of sulphur dioxide at N.T.P. *O.C. (part)*

7. State Avogadro's hypothesis. If one volume of hydrogen combines with one volume of chlorine to give two volumes of hydrogen chloride (all measured at the same temperature and pressure) deduce the simplest formulæ for molecules of hydrogen, chlorine and hydrogen chloride. *J.M.B.*

8. State Avogadro's hypothesis and show how it explains the facts embodied in Gay-Lussac's law of volumes. From density determinations it is known that 10 c.c. of a certain gas 'G' weigh as much as 140 c.c. of hydrogen, under the same temperature and pressure conditions. Calculate the molecular weight of 'G.' *Dur.*

9. Define the terms 'vapour density' and 'molecular weight.'

From your definitions deduce the relation existing between vapour density and molecular weight, stating any assumptions which you have made in your deduction.

Assuming that air consists of 20 per cent. oxygen and 80 per cent. nitrogen by volume, show that the vapour density of air is 14·4. *Lond.*

10. Describe carefully Victor Meyer's method for the determination of vapour density.

The vapour densities of the chloride and bromide of an element of fixed valency are 85 and 174 respectively. Calculate the atomic weight and valency of the element. *O.C. Alt. (part)*

11. Explain briefly how the atomic weight of an element may be found by determining the molecular weights of several compounds of it and the percentage weight of the element in these compounds.

Three compounds of a certain element contain 42·85, 27·25 and 92·3 per cent. of the element. The respective vapour densities of these compounds are 14, 22 and 39 compared with that of hydrogen. What is the probable atomic weight of the element? *Oxf.*

B

N.B. *The 'B' questions which follow require a knowledge of certain chemical changes which up to this point have not been studied. It will be well therefore to leave them until the work is being gone through for a second time.*

1. Calculate the vapour densities of hydrogen chloride, chlorine, nitrogen and water vapour.

2. Arrange the following gases in ascending order of density: hydrogen sulphide, chlorine, carbon dioxide, argon, nitric oxide, acetylene. (*N.B.* The molecule of argon is monatomic.)

3. What volume of carbon monoxide, at N.T.P., would be used in reducing 1 gm. of cupric oxide to copper? *Dur.* (*part*)

4. What volume of the constituent gases would be present in *v* c.c. of nitrous oxide, hydrogen chloride and steam respectively?

5. State Avogadro's rule and use it to deduce the relation between the molecular weight and the vapour density of a gas.

What volume of air (20 per cent. oxygen) is needed for the complete combustion of 100 c.c. of water gas, $H_2 + CO$, and what are the volumes and natures of each of the resulting gases if all measurements are made (*a*) above 100° C.; (*b*) at room temperature? *Oxf.*

6. (i) What volume of hydrogen at N.T.P. could be obtained by dissolving 1·2 gm. of magnesium in dilute acid?

(ii) What volume of oxygen at N.T.P. could be obtained by heating 1·225 gm. of potassium chlorate to constant weight?

(iii) What volume of what gas would be left at N.T.P. if these volumes of hydrogen and oxygen were mixed and exploded? *Oxf.* (*part*)

7. (*a*) State (i) Avogadro's law, (ii) Gay-Lussac's law.

(*b*) 10 c.c. of each of the following gases were burned in excess of oxygen: carbon monoxide, hydrogen sulphide. Calculate the volume of oxygen consumed and the volume of the product in each case. All volumes were measured at N.T.P. *O.C.* (*part*)

8. What volume of oxygen, measured at N.T.P., can be obtained by completely decomposing 4·9 gm. of potassium chlorate? *W.J.* (*part*)

9. A measured volume of air was passed through excess of lime-water. The weight of the dried precipitate of calcium carbonate was 0·2 gm. and the volume of air was 100 litres when measured at N.T.P. Calculate (i) the weight, (ii) the volume of carbon dioxide present in the 100 litres of air. *W.J.*

10. State fully Gay-Lussac's law of combining volumes.

Write equations for (*a*) the explosion of hydrogen and oxygen; (*b*) the synthesis of ammonia from nitrogen and hydrogen.

If all volumes are measured at N.T.P., state the volume and the name of the gas remaining when (i) 200 ml. of hydrogen are exploded with 500 ml. of oxygen, (ii) 300 ml. of hydrogen combine completely with 100 ml. of nitrogen. *J.M.B.*

11. 10 c.c. of a gaseous hydrocarbon C_xH_4 required 30 c.c. of oxygen for complete combustion. What is x? *O.C.* (*part*)

12. Establish the relation between the molecular weight and the vapour density of a compound.

Describe in detail an experiment to determine the vapour density of a volatile compound.

A volatile compound of hydrogen, carbon and oxygen has a vapour density of 37. When 1·11 gm. of this compound was passed through heated copper oxide, 1·35 gm. of water and 2·64 gm. of carbon dioxide were formed. Calculate the molecular formula of the compound. *Scot.L.C.*

13. State the law expressing the combination of gases by volume, and describe an experiment which demonstrates the law in the case of the combination of hydrogen and chlorine.

5 c.c. of a gas, containing *only* carbon and hydrogen, required 15 c.c. of oxygen for complete combustion, and 10 c.c. of carbon dioxide was formed. All volumes were at the same temperature and pressure. What is the molecular formula of the gas? *Dur.*

14. State Avogadro's law, and use it to deduce the relationship that exists between the vapour density of a gas and its molecular weight. (You may assume that a molecule of hydrogen contains two atoms.)

When 50 gm. of a solid are heated, the residue weighs 2·8 gm., and 1120 c.c. of a gas, measured at 0° C. and 760 mm., are evolved. What is the molecular weight of the gas? *Camb.*

CHAPTER 12

DIFFUSION OF GASES

To illustrate the fact that carbon dioxide is a heavy gas we may 'pour' it over a lighted taper, which is soon extinguished. To show that hydrogen is lighter than air we may collect two jars of it and hold one of them mouth upwards for about 15 seconds, holding the other mouth downwards for the same time. On testing with a lighted taper we find that the second one 'pops' but the first does not. Evidently hydrogen finds it easier to escape *upwards* than to escape *downwards*.

The results so far are pretty much what we should expect. But consider the experiment illustrated in fig. 12/1, where jars of hydrogen and oxygen are placed mouth to mouth, the hydrogen being on the *top*. If the jars are tested at the end of a quarter of an hour or so, *both* of them are found to contain an explosive mixture. This shows that it is quite possible for a light gas to move downwards and for a heavier gas to move upwards. The fact is that *a gas distributes itself through the whole of the space offered to it, although this space may be occupied by another gas*; and this property is known as ***diffusion.***

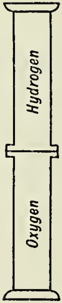

FIG. 12/1

Examples of gaseous diffusion are very common. Somebody accidentally knocks a gas-tap in the laboratory, and the smell of gas is soon noticed several yards away. In hot weather the stopper of a Winchester quart bottle of ammonia sometimes blows off, and the smell of ammonia is soon very perceptible.

When we remember that a gas consists of molecules moving about with great speed we can easily account for diffusion. Think of the upper jar (hydrogen) in fig. 12/1. The molecules are travelling with a very high average speed. They 'shoot' in all directions, and are naturally soon found in the lower jar. They would make their way there very much faster only for the fact that they are constantly colliding with other molecules. Given a clear field, a boy may be able to run at ten miles an hour, but if he is in the middle of a crowd his speed is very much less, however anxious he may be to get through.

Some of the facts considered so far may seem contradictory, e.g. (i) hydrogen escapes upwards more easily than it escapes downwards, and yet (ii) it makes its way into the lower jar in the experiment illustrated by fig. 12/1. We may describe (i) as the 'gravity effect,' (ii) as the 'diffusion effect.' Perhaps an illustration will help to clear up the difficulty. Think of a man sitting among the rafters of a barn and holding a swarm of bees in his arms (an unusual situation certainly, but the illustration will serve our turn). For our purpose too, let us suppose that the bees, instead of being dominated by the 'swarming' instinct, are most anxious to make excursions of their own at top speed. The man now lets the swarm fall, and we can distinguish two effects. Speaking generally, the swarm moves bodily downwards (gravity effect); but a good number of bees, mostly those on the outskirts of the swarm, make their way to all parts of the barn (diffusion effect). A little later the bees struggling near the floor have succeeded in following their example. In the same way we can pour a heavy gas, such as carbon dioxide, downwards, but after a while the molecules will make their way to the very limits of the space open to them.

Important experiments on the diffusion of gases were made by Thomas Graham in 1832. In some of them he enclosed his gases in bottles, through the cork of which there passed a long glass tube. If the gas was heavier than air he held the tube upwards, and vice versa—he wanted to avoid the gravity effect. After a measured interval of time he would analyse the contents of the bottle and find how much gas had escaped. He summed up his results in the following statement, which is known as ***Graham's Law of Diffusion.*** *The rate at which a gas diffuses is inversely proportional to the square root of its density.*

As an illustration let us take the cases of oxygen and hydrogen. If the density of hydrogen is represented by 1, that of oxygen will be 16. (The density, remember, is half the molecular weight, p. 126.) Thus Graham's Law tells us that

$$\frac{\text{rate for hydrogen}}{\text{rate for oxygen}} = \frac{\sqrt{\text{density of oxygen}}}{\sqrt{\text{density of hydrogen}}} = \frac{\sqrt{16}}{\sqrt{1}} = \frac{4}{1}.$$

Note that the 'rate for hydrogen' comes in the *numerator* of one fraction, and '$\sqrt{\text{density of hydrogen}}$' in the *denominator* of the other. That is because the rate varies *inversely* as $\sqrt{\text{density}}$.

Experimental Illustrations. We have already had illustrations of the fact that gases diffuse (accidental turning on of gas-tap; smell of ammonia; jar of hydrogen over jar of oxygen). We shall now consider one or two illustrations of the fact that a light gas diffuses more rapidly than a heavy one.

In fig. 12/2 AB is a tube about a yard long dipping into a beaker of water. The upper end of the tube fits into a porous pot closed with a cork. The bell-jar, C, is filled with coal-gas[1] and then placed over the porous pot. Bubbles rapidly escape from the bottom of the tube, because coal-gas diffuses *into* the porous pot more rapidly than the heavier air diffuses *out* of it. Thus there is an increase in the number of molecules inside the pot and therefore in the pressure. On removing the bell-jar, coal-gas diffuses outwards, more rapidly than air diffuses in, and water rises in the tube.

An interesting variation of the experiment is shown in fig. 12/3. The terminals of an electric-bell circuit are fused into a U-tube at E and F. Mercury is poured into the tube until it reaches D, a point a little below F. It will be clear from the figure that when the jar of coal-gas is placed over the porous pot the circuit is completed and the bell rings.

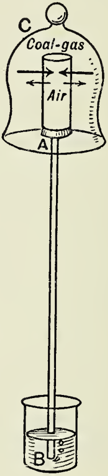

FIG. 12/2. Coal-gas diffuses more rapidly than air

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[1] Hydrogen gives rather better results, but coal-gas is usually more convenient.

For experiments with gases heavier than air (e.g. carbon dioxide), the tube should be so bent that the bell-jar can be placed *under* the porous pot.

If an explosive mixture of hydrogen and oxygen (conveniently prepared as indicated in fig. 9/9*a* on p. 103) is passed through a long pipe-clay tube, oxygen practically free from hydrogen can be collected at the other end.

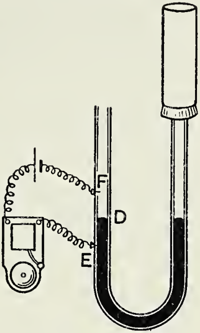

FIG. 12/3

The following is another instructive experiment.[1] A and B (fig. 12/4) are crucibles resting on cover-slips (rough side upwards, and greased so that later they will grip closely to a gas-jar). Each contains a little bromine.

Two gas-jars are dried, and one is filled with hydrogen by displacement of air. This is inverted over B, while the other one, containing air, is inverted over A. In each case the heavy brown vapour of bromine can be seen in the crucible, slowly spreading into the jar.

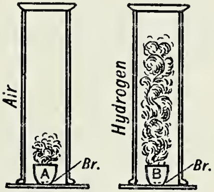

FIG. 12/4
Hydrogen diffuses more rapidly than air

Now as bromine vapour is much heavier than either air or hydrogen, it would remain at the bottom if the 'gravity' effect were the only one. Actually

(i) it rises in both jars, and

(ii) it rises much faster in the hydrogen jar.

This shows that

(i) Diffusion is taking place in both jars, a heavier gas (bromine) moving upwards and a lighter one (air or hydrogen) moving downwards.

(ii) Hydrogen diffuses more rapidly than air.

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[1] Adapted from Ostwald's *Principles of Inorganic Chemistry.* He uses jars only, but it is very difficult to place bromine at the bottom of these without distributing some vapour in the process.

Calculations. In working out calculations on diffusion of gases, it is better to express Graham's Law in a slightly different form, viz. *The time which a gas takes to diffuse is directly proportional to the square root of its density.* This follows because time varies inversely as rate, i.e. $t \propto \frac{1}{r}$, and rate varies inversely as $\sqrt{\text{density}}$, i.e. $r \propto \frac{1}{\sqrt{d}}$, or $\frac{1}{r} \propto \sqrt{d}$.

But $t \propto \frac{1}{r}$. $\therefore t \propto \sqrt{d}$, i.e. time varies directly as $\sqrt{\text{density}}$.

Thus if two gases have densities d_1 and d_2 respectively, and t_1 and t_2 are the times which equal volumes of them take to diffuse

$$\frac{t_1}{t_2} = \frac{\sqrt{d_1}}{\sqrt{d_2}}.$$

Example 1. *Equal volumes of two gases diffuse through a porous plug in* 8 *and* 32 *minutes respectively. What relationship exists between their molecular weights?* Lond.

Let their molecular weights be m_1 and m_2. Then their densities relative to hydrogen are given by $d_1 = \frac{1}{2}m_1$ and $d_2 = \frac{1}{2}m_2$ (p. 126).

Now
$$\frac{t_1}{t_2} = \frac{\sqrt{d_1}}{\sqrt{d_2}}.$$

$$\therefore \frac{8}{32} = \frac{\sqrt{d_1}}{\sqrt{d_2}}.$$

$$\therefore \frac{\sqrt{d_1}}{\sqrt{d_2}} = \frac{1}{4}, \quad \text{whence} \quad \frac{d_1}{d_2} = \frac{1}{16}.$$

$$\therefore \frac{\frac{1}{2}m_1}{\frac{1}{2}m_2} = \frac{1}{16}, \quad \text{or} \quad \frac{m_1}{m_2} = \frac{1}{16}.$$

Thus the molecular weight of the second gas is sixteen times that of the first.

Example 2. 400 *c.c. of hydrogen diffuse through a porous plate in* 16 *seconds. How long would it take* 250 *c.c. of carbon dioxide to diffuse through the same plate?*

Molecular weight of carbon dioxide, CO_2, $= 12 + 32 = 44$.
$\therefore$ its density relative to hydrogen $= 22$.

To begin with, consider the same volume (400 c.c.) in each case.

Then $$\frac{t_c}{t_h}=\frac{\sqrt{d_c}}{\sqrt{d_h}}.$$

Where t_c = time for carbon dioxide,
t_h = time for hydrogen, etc.

$$\therefore \frac{t_c}{16}=\frac{\sqrt{22}}{\sqrt{1}}.$$

$$\therefore t_c=16\times\sqrt{22}=16\times 4{\cdot}69=75{\cdot}0 \text{ seconds.}$$

This is the time for 400 c.c. of carbon dioxide.

$$\therefore \text{time for 250 c.c.}=\frac{250}{400}\times 75{\cdot}0=\boldsymbol{46{\cdot}9 \text{ seconds.}}$$

Questions

1. Why does hydrogen slowly escape from a gas-jar held mouth downwards, although it is lighter than air? *Oxf. (part)*

2. State Graham's *Law of Diffusion* of Gases, and describe any experiments you have witnessed relating to diffusion of gases. In 50 seconds 300 c.c. of oxygen diffuse through a porous plate. How long will it take 500 c.c. of chlorine to diffuse through the same plate? (Take the molecular weights of oxygen and chlorine as 32 and 72 respectively.) *Lond.*

3. Describe, with a diagram of apparatus, how you would show that hydrogen diffuses more rapidly than air. *J.M.B. (part)*

4. If a mixture of hydrogen and oxygen be passed through a long pipe-clay tube and collected over water, oxygen containing little or no hydrogen is obtained. Explain clearly the reason for this and draw a diagram of the apparatus by means of which you could demonstrate the correctness of your explanation. *Oxf. (part)*

5. Describe, with equations, experiments by which you have prepared and collected hydrogen using (*a*) an acid, and (*b*) an alkali.

State *Graham's law of diffusion.*

In 150 seconds 900 ml. of oxygen diffuse through a porous plug. If it takes 125 seconds for 500 ml. of another gas X to diffuse through the same plug under the same conditions, what is the molecular weight of X? (Assume the vapour density of oxygen to be 16.) *J.M.B. (Alt.)*

6. In 1868 Soret found that if the rate of diffusion of carbon dioxide were represented by the number 290, that of ozone was represented by 271. What value does this give for (*a*) the density of ozone, (*b*) its molecular weight?

7. If the rate of diffusion of the fluoride of U^{238} ($U^{238}F_6$) is represented by the number 100, what number would represent that of the fluoride of U^{235} ($U^{235}F_6$)? (Answer to two places of decimals.)

N.B. The atomic weights of U^{238} and U^{235} are 238 and 235 respectively.

CHAPTER 13

OXYGEN

Occurrence. Oxygen is present *free* in the air to the extent of 21 per cent. by volume (or 23 per cent. by weight), and *in combination* in water to the extent of 89 per cent. by weight. The earth's crust consists largely of compounds containing oxygen, and it is estimated that about 50 per cent. of its weight is due to the presence of this element.

History. Joseph Priestley is usually regarded as the discoverer of oxygen. He obtained it in 1774 by heating mercuric oxide with the help of a large burning-glass, and we have already seen that Lavoisier was able to turn the discovery to good account.

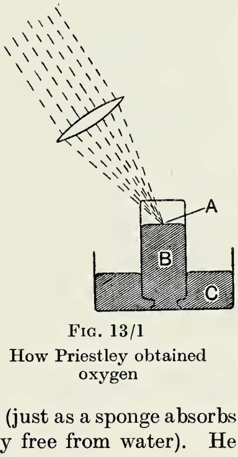

FIG. 13/1
How Priestley obtained oxygen

Actually the Swedish chemist Scheele had obtained oxygen at least a year earlier than Priestley, but as the English chemist knew nothing of Scheele's work he is entitled to almost equal credit.

From Priestley's point of view, a substance burning freely in oxygen was simply *losing its phlogiston* at a great rate. He argued that since the new gas absorbed phlogiston so readily, it must itself be very free from this peculiar substance (just as a sponge absorbs water freely only if it was previously free from water). He therefore called the new gas *dephlogisticated air*.

Lavoisier burned sulphur in the gas, and found that when the product was dissolved in water an acid was formed. He obtained similar results with carbon, phosphorus, etc., and came to the conclusion that this gas is essential to the production of acids. That is why he gave it the name *oxygène* (from two Greek words meaning 'acid producer'). We now know that many acids (e.g. hydrochloric acid, HCl) do not contain any oxygen, so the name is not very suitable.

Preparation. (1) Oxygen can be prepared from the air by heating mercury until it is oxidised, and then decomposing the mercuric oxide. The experiment is often carried out by means of the apparatus sketched in fig. 13/2. On heating, the hot air escapes through the tube CD, and is replaced by fresh air drawn in through the tube AB. Thus a current of fresh air is constantly sweeping over the surface of the mercury. The ideal temperature is about 350° C. (i.e. just below the boiling-point of mercury, which is 357° C.). This is recorded by the thermometer, T.

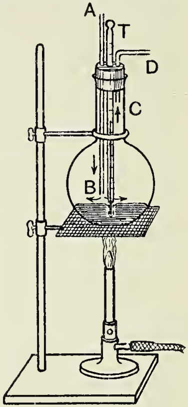

Fig. 13/2
Oxidation of mercury

After about a week the dark-coloured oxide is skimmed off and transferred to a test-tube, which is heated as shown (for another substance) in fig. 13/3.

It will be obvious that this method is laborious in the extreme, and it is only described here because of its great historical importance (mercuric oxide having been used so much by Priestley and Lavoisier).

The equation for the preparation of mercuric oxide would be

$$2Hg + O_2 = 2HgO$$

and for its decomposition

$$2HgO = 2Hg + O_2$$

[*Q.* If O_2, why not Hg_2?]

(2) The usual laboratory method is to heat potassium chlorate with about a quarter its weight of manganese dioxide

$$\begin{array}{cccc} [KClO_3 & = & KCl & +3O] \\ 2KClO_3 & = & 2KCl & +3O_2 \\ \text{Potassium chlor}\textit{ate} & & \text{Potassium chlor}\textit{ide} & \end{array}$$

It will be seen that the manganese dioxide (MnO_2) does not appear in the equation, and indeed when the action is over, it can be extracted from the residue in the test-tube unchanged in quantity or in properties. Yet the oxygen comes off far more easily (though *not* in larger quantity) when the manganese dioxide is present than when it is not.

The manganese dioxide is said to be a ***catalyst*** or ***catalytic agent***, i.e. *a substance which alters the rate at which a chemical action proceeds without itself undergoing any permanent change.* The subject of catalysis will be further considered on p. 288.

(3) The oxygen obtained by the 'potassium-chlorate' method is not very pure. Pure oxygen may be prepared in the laboratory by the action of water on sodium peroxide:—

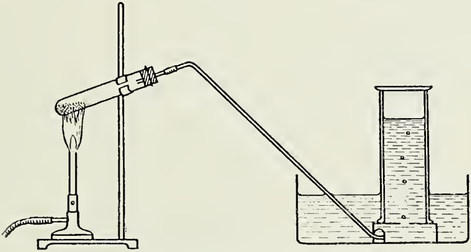

FIG. 13/3. Oxygen from potassium chlorate

$[Na_2O_2 + H_2O = 2NaOH + O]$ $2Na_2O_2 + 2H_2O = 4NaOH + O_2$

The peroxide is placed in a flask, and water is slowly run on to it from a dropping funnel as indicated in fig. 13/4.

(*N.B.* Sodium peroxide is manufactured by heating sodium in a current of dry air, so that when we use it to obtain oxygen we are indirectly obtaining oxygen from the air.)

(4) On the large scale, oxygen is obtained either (i) from the air, or (ii) from water.

Oxygen from the Air. Carbon dioxide and water vapour must first be removed, because at the low temperatures attained during subsequent operations, these would solidify and block tubes, valves, etc. The air, after being filtered, compressed and cooled,[a] is passed upwards through a tower, where it meets a descending spray of caustic soda solution. This removes carbon dioxide (p. 178). It then passes through a second, smaller tower containing solid caustic soda, which removes water vapour (p. 416).

The air is now liquefied. The principle employed is that if a gas under pressure is allowed to expand, it becomes cooler as it does so (for instance, the air escaping from a puncture in a bicycle tyre 'strikes cold' against one's face).

Suppose we have two copper spiral tubes, one inside the other. Compressed air from the inner spiral is allowed to expand through the valve V, and is thus cooled. For the sake of clearness, suppose the air was originally at 0° C. and is now cooled to $-5°$ C. This cooler air now passes through the outer spiral, with the result that the oncoming air in the inner spiral is cooled to $-5°$ C.[1] By expansion through the valve it is further cooled to $-10°$, after which it flows through the outer spiral, still further cooling the air in the inner one; and so on. After a short time—usually from six to ten minutes—the temperature will have fallen so much that the air liquefies as it passes through the valve.

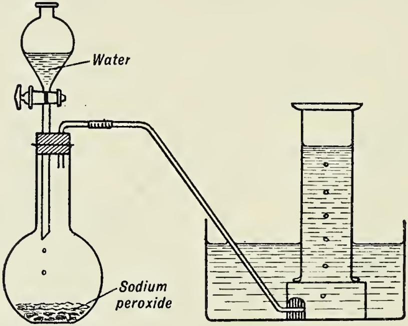

FIG. 13/4. Oxygen from sodium peroxide

To obtain oxygen from the liquid air, advantage is taken of the fact that the boiling point of nitrogen (– 196° C.) is lower than that of oxygen (– 183° C.), so that liquid nitrogen will vaporise more freely than liquid oxygen. Thus the vapour given off from the liquid air contains more than the normal 79 per cent. of nitrogen, while the liquid left behind contains more than 21 per cent. of oxygen. By an ingenious contrivance it has been found possible to carry this separation further and further, until oxygen of about 99 per cent. purity is obtained. This is packed into steel cylinders at a pressure of 120 atmospheres and marketed.

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[1] Actually the temperature would be somewhere between 0° and $-5°$, but it is not desirable to complicate the argument.

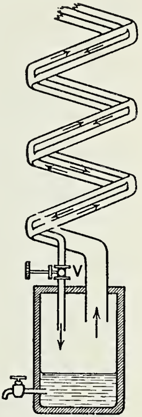

Fig. 13/5
Liquefaction of air

The other constituent, rich in nitrogen and very cold, is used for cooling the incoming stream of air (see (*a*), p. 145), and is then allowed to escape into the atmosphere. Similarly, if nitrogen is being extracted from the air, the oxygen-rich constituent is allowed to escape.

Oxygen from Water. In the chapter on Hydrogen we saw that in the oil and fat industry there is a great demand for hydrogen of a high degree of purity, and that this hydrogen is often obtained by the 'electrolysis of water.' Oxygen is, of course, obtained at the same time, and as this oxygen is likewise very pure it finds a ready market.[1]

Uses. When Priestley tried the effect of breathing one of his first specimens of oxygen, he reported, 'I fancied that my breast felt peculiarly light and easy for some time afterwards.'

In these words we have a suggestion of one of the present-day uses of oxygen, which is often administered by medical men. Sometimes this is done by means of an 'oxygen tent,' as shown in the illustration over-leaf.

Only about 2 per cent., however, of all the oxygen manufactured is used in this way. Much the greater part of it—about 80 per cent.—is used for oxy-acetylene welding and steel-cutting, and about 18 per cent. for other work among metals.

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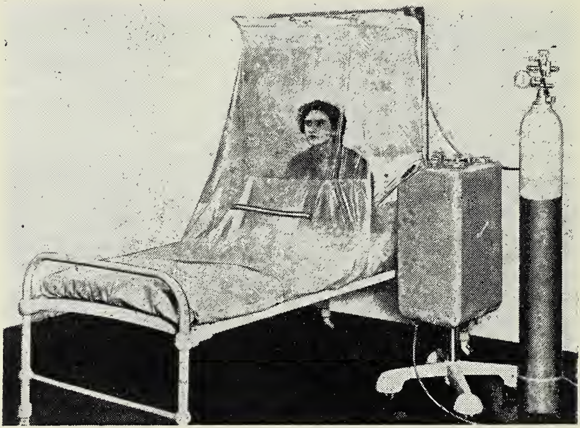
[1] Not always. Electrolysis on the large scale is often carried on near waterfalls, etc., so that electric power can be generated cheaply. In such districts it frequently happens that there are no industries requiring a supply of oxygen, and in view of the high cost of transit it is allowed to escape to the air.

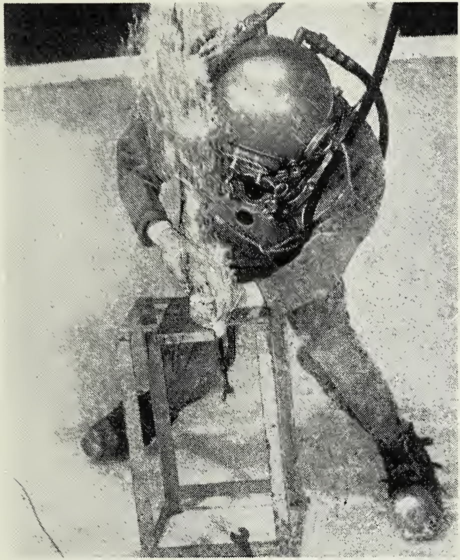
You can easily see oxy-acetylene welding carried on in a garage where much repair work is done. A flame of acetylene is fed with oxygen, and in certain parts the extraordinary temperature of 4400° C. is attained.



By courtesy of Oxygenaire (London) Ltd.

Oxygen tent

Steel-cutting depends on the fact that iron will burn in oxygen (forming the oxide, Fe_3O_4). The heat produced by this chemical action is sufficient to cause the next portion of metal to burn, so that theoretically the process is continuous once it has been started. In practice, it is found necessary to use an extra source of heat (usually an acetylene flame, but a hydrogen flame is preferred for work under water). One purpose thus served is that at the higher temperatures attained in this way, the oxide of iron is kept fluid and is continuously swept away by the blast. Some idea of the possibilities of oxygen cutting will be gained from the illustrations on this page and on p. 201. A good machine on a 'straight' job will cut a 3-inch steel plate at the rate of 34 feet per hour, or if patterns have to be followed, as in the illustration on p. 201, at 20 feet per hour. Most varied work can be undertaken. For instance, some time ago the entire after-part of a large ship was cut off, just as one might cut through a toy boat with a saw. The accompanying photograph shows a diver using the oxy-hydrogen flame for cutting steel *under water*.



By courtesy of Messrs. Siebe, Gorman & Co. Ltd.

Diver using oxy-hydrogen torch under water

Oxides. One of the chief properties of oxygen is that it combines with most other elements, forming oxides. In the laboratory you have no doubt prepared (or seen prepared) the oxides of carbon, sulphur, phosphorus, magnesium, sodium, iron, zinc, calcium, etc., by first heating a little of the element in a deflagrating spoon and then plunging it into a jar of oxygen.

The elements mentioned—in fact, nearly all elements—can be placed in one or other of the two classes, *metals* and *non-metals.* In a rough and ready way we can usually recognise a metal by its shiny appearance ('metallic lustre'), and by the fact that when struck, or allowed to fall, it gives out a ringing sound. A metal, too, is usually a good conductor of heat and of electricity, and has a high density. There are exceptions unfortunately (sodium, for instance, has such a low density that it floats on water), but the rules are fairly general.

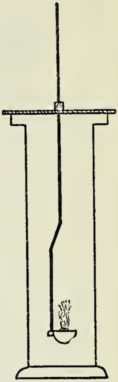


FIG. 13/6 Preparation of oxides

Now there is a very important difference between the oxides of metals and the oxides of non-metals. *Oxides of non-metals combine with water to form acids.* An acid can often be detected by its sour taste, but, of course, it would never do to go testing substances in this way. Instead, we use litmus—acids turn litmus solution red. Oxides of non-metals are, therefore, often called ***acid-forming oxides***, or ***acidic oxides***. Sometimes they are called ***anhydrides***, which comes from two Greek words meaning 'without water.' The idea is that as a non-metallic oxide does not become an acid until water is added to it, it is therefore an acid without water. Such oxides are sometimes named with reference to the acids they give when treated with water. For instance, sulphuric dioxide is sometimes called *sulphurous anhydride* because on treatment with water it yields sulphurous acid. Similarly we have *phosphoric anhydride*, related to phosphoric acid, and so on.

Of the elements mentioned above, carbon, sulphur and phosphorus (all non-metals) form the kind of oxide we have just been describing. In each case the oxide, on the addition of water, forms an acid, and this turns litmus paper red.[1]

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[1] Methods of distinguishing between the various classes of oxides are fully described on pp. 177–180 of the author's *School Course of Practical Chemistry* (Bell).

Now, just as we can use a non-metallic oxide to *make* an acid, we can use a metallic oxide to *unmake* one—to *neutralise* it, as we say.

The oxide of a metal is known as a ***base*** (or ***basic oxide***). A base, then, will neutralise an acid. The neutral substance produced when it does so is called a ***salt.*** It can be proved that *water* is also produced at the same time. Summing up all this, we have

Base + Acid = Salt + Water

Going back to the elements mentioned above, we find that magnesium, sodium, iron, zinc and calcium all give basic oxides—oxides that will neutralise acids. To get all this quite clear let us take a particular case:

(i) *Carbon* (a non-metal) gives *carbon dioxide* (an acid-forming oxide). *Carbon dioxide* combines with *water*, giving an acid (*carbonic acid*):—

$$C + O_2 = CO_2$$
$$CO_2 + H_2O = H_2CO_3$$

(ii) *Calcium* (a metal) gives *calcium oxide* (a basic oxide):—

$$[Ca + O = CaO] \qquad 2Ca + O_2 = 2CaO$$

(iii) *Calcium oxide + carbonic acid = calcium carbonate* (a salt) + *water*:—

$$CaO + H_2CO_3 = CaCO_3 + H_2O$$

We have seen that the solution of an anhydride (i.e. oxide of a non-metal) turns litmus red. Basic oxides are often insoluble in water, and in that case they have no effect on litmus. When they *do* dissolve, the solution turns litmus paper blue. Strictly, the basic oxide does not simply dissolve, but combines with the elements of water, forming what is called a *hydroxide*, e.g. $Na_2O + H_2O = 2NaOH$. ($NaOH$ = *sodium hydroxide*.) It is really the solution of this hydroxide which turns litmus blue, or is 'alkaline to litmus' as we say, a soluble hydroxide being called an *alkali*.

(Insoluble hydroxides can easily be prepared, but *not* by adding water to the corresponding basic oxide. An insoluble hydroxide—e.g. copper hydroxide, $Cu(OH)_2$—has no effect on litmus, and would not be called an alkali.)

The two classes of oxide just considered (anhydrides and bases) are by far the most important, but there are some others which we must not overlook. First, there are a few —aluminium oxide, Al_2O_3, is an example—which act sometimes as anhydrides, sometimes as bases. They are known as *amphoteric* oxides (Gk. *amphoteros*=both).

Then there are some oxides of metals which contain two atoms of oxygen in the molecule, where from the usual valency of the element we should expect only one. Thus from barium, Ba, and lead, Pb (both divalent), we should expect oxides of the formulæ BaO and PbO. These actually exist, but we have also BaO_2 and PbO_2.

Some of these 'higher' oxides yield hydrogen peroxide when treated with a cold dilute acid (p. 160), and are known as ***peroxides*** ; e.g. BaO_2 is the formula of barium peroxide. If they do not behave in this way they are described as ***dioxides.*** Thus PbO_2 is the formula of lead dioxide.

While peroxides and dioxides of metals differ in the way just mentioned, they are alike in that

(i) when heated alone, or with sulphuric acid, they give off oxygen (e.g. $2PbO_2 = 2PbO + O_2$), and

(ii) when heated with hydrochloric acid, chlorine is evolved (p. 248).

Lastly, we must notice a few ***neutral oxides,*** which fall into none of the above classes. Examples are: water, H_2O, and nitric oxide, NO.

Acids and Salts. We have seen that a salt is produced when a basic oxide reacts with an acid, e.g.

$$CaO + H_2SO_4 = CaSO_4 + H_2O$$

It will be convenient at this point to go more thoroughly into the question of salt-formation.

We must begin with the term *acid.* It is not of much use to say that 'an acid is the substance formed when the oxide of a non-metal is dissolved in water,' because though acids are often formed in this way, there are some acids which do not contain oxygen at all—hydrochloric acid (HCl) for instance. All acids, however, contain hydrogen, and for our present purpose it will be near enough if we say that an acid is a compound containing hydrogen, some or all of which is replaced by a metal when the compound is treated with a metallic oxide or hydroxide, the products being a salt and water. The statement may be illustrated by the equation

$$HCl + NaOH = NaCl + H_2O$$

*A **salt** is the substance formed when the hydrogen of an acid is replaced by a metal*, e.g. the equation just given shows that the salt sodium chloride is formed when the hydrogen of hydrochloric acid is replaced by sodium.

We may look at salts in another way, once again making acids our starting-point. That part of the molecule of an acid *other than the hydrogen* is often called the 'acid radical.' Thus in sulphuric acid, H_2SO_4, the acid radical is SO_4; in nitric acid, HNO_3, it is NO_3 and so on. With this in mind we may say that a ***salt*** is *a compound of a metal with an acid radical.*

General Methods for Preparing Salts. Salts may be prepared (1) By the action of an acid on a *metal*, or on the *oxide*, *hydroxide* or *carbonate* of the metal.

Thus zinc sulphate might be made by the action of sulphuric acid on zinc, or on the oxide, hydroxide or carbonate of zinc. The equations would be

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$
$$ZnO + H_2SO_4 = ZnSO_4 + H_2O$$
$$Zn(OH)_2 + H_2SO_4 = ZnSO_4 + 2H_2O$$
$$ZnCO_3 + H_2SO_4 = ZnSO_4 + H_2O + CO_2$$

(2) An insoluble salt is readily made by *double decomposition.*[1] Suppose, for instance, we wish to make calcium carbonate, $CaCO_3$. We may take a *soluble* calcium salt such as the chloride ($CaCl_2$) and a *soluble* carbonate such as sodium carbonate, and add one solution to the other. Calcium carbonate is precipitated, and is readily filtered, washed and dried:—

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$$

---

[1] I.e. a chemical change of the type $AX + BY = AY + BX$. In the present case A is represented by Ca, X by Cl_2, B by Na_2 and Y by CO_3.

(3) A salt may sometimes be made by the action of an acidic oxide on a basic oxide. Thus, if calcium oxide (quicklime, CaO) is exposed to carbon dioxide, CO_2, calcium carbonate is gradually formed:—

$$CaO + CO_2 = CaCO_3$$

The method is not of much practical importance, but is interesting because it shows that a salt may often be regarded as a compound of a basic oxide with an acidic one.

(4) Salts which consist of only two elements may often be made by simply heating the elements together. Thus ferrous sulphide may be made by heating iron with sulphur,

$$Fe + S = FeS$$

and sodium chloride by heating sodium in chlorine,

$$2Na + Cl_2 = 2NaCl$$

Questions

1. Say what you know of (i) Joseph Priestley, (ii) Antoine Laurent Lavoisier.

2. Explain carefully why the results of Lavoisier's twofold experiment (i.e. the formation and, later, the decomposition of mercuric oxide) are exactly opposite to what the phlogistic theory would lead us to expect.

3. What volume of oxygen at N.T.P. could be obtained by heating 12·25 gm. of potassium chlorate?

($K=39$; $Cl=35{\cdot}5$; $O=16$. Gram-molecular volume$=22{\cdot}4$ litres.)

4. Name *three* substances which on heating evolve oxygen, and give equations for the reactions which occur.

State briefly, without technical details, how oxygen may be produced from air.

Name *two* important everyday uses of oxygen. *Lond.* (*part*)

5. Give, with the equation, a fully labelled sketch to show how you would prepare and collect gas-jars of oxygen.

Sodium and sulphur are burnt in separate jars of oxygen, and in each case the product is afterwards shaken up with purple litmus solution. Describe what you would *see*, and give brief explanations of the changes which have taken place. *J.M.B.*

6. Explain what is meant by a base. Give *three* examples of bases. Describe fully how you would prepare a specimen of a base, starting from copper, and describe an experiment to demonstrate that this substance really is a base. *Camb.*

7. A certain solid oxide XO_2 contains $53\frac{1}{3}\%$ of oxygen. Find (*a*) the equivalent weight of X, (*b*) the valency of X, (*c*) the atomic weight of X.

When this oxide XO_2 is heated with sodium carbonate, a gas is given off which turns lime-water milky. State whether the oxide XO_2 is basic or acidic, and give your reasons for believing that the element X is probably a non-metal. *J.M.B.*

8. You are asked to find by three different tests whether a certain substance is an acid. Describe the tests you would apply, and the results you would expect to observe.

9. Describe briefly *four* different methods of preparing salts in the laboratory. Use as examples *four* of the following: ammonium sulphate, zinc sulphate, lead nitrate, calcium chloride, copper carbonate, ferric chloride. *Camb.*

CHAPTER 14

OZONE AND HYDROGEN PEROXIDE

OZONE

OZONE is produced when oxygen is submitted to what is called the silent electric discharge. Various forms of 'ozoniser' are in use. One of the best, known as Brodie's, is shown in fig. 14/1. It will be seen that one glass tube is fixed within another. The inner tube contains dilute sulphuric acid, which is thus separated from a larger quantity of the same liquid surrounding the outer tube. Through a length of platinum wire dipping into it, the inner portion of acid is in electrical connection with one terminal of an induction coil, and the outer portion is similarly connected with the other terminal. A slow stream of oxygen passing through the annular space between the two tubes is thus subjected to electric stress, and on emerging may contain as much as 25 per cent. of ozone, though the yield is usually much less.

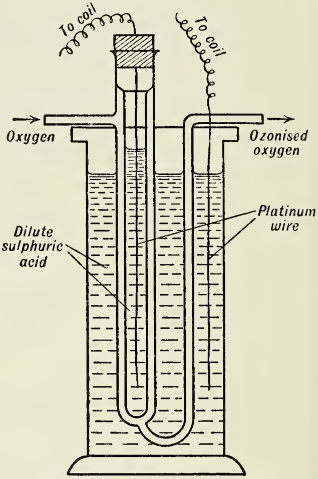

FIG. 14/1. Production of ozone

Properties. The smell of greatly diluted ozone (easily noticed when an electric machine is working) is rather suggestive of chlorine. Ozone is much less soluble in water than is oxygen.

If ozonised air is passed into a clean flask containing mercury, the latter 'tails,' i.e. it clings to the glass as though it were dirty. No doubt this is due to the metal being superficially oxidised. The powerful oxidising action of ozone is also shown by its action on starch-iodide paper (i.e. paper which has been dipped in a mixture of starch and potassium iodide). The starch is quickly turned blue by the iodine liberated from the potassium iodide[1]

$$2KI + O_3 + H_2O = 2KOH + O_2 + I_2$$

When passed through a tube heated to 400° C. ozone loses its smell and no longer acts upon starch-iodide paper. It has, in fact, been converted into ordinary oxygen

$$2O_3 = 3O_2$$

Composition. Since ozone is made from oxygen only (by electrical action) and is converted into oxygen only (by heat), it seems clear that ozone is a form of oxygen. How are we to account for the existence of two forms of the same element?

Pure ozone is a substance by no means easy to obtain. However, it *has* been obtained, and has been found to have a vapour density of 24 (i.e. it is 24 times as heavy as an equal volume of hydrogen measured under similar conditions). The vapour density being 24, the molecular weight must be 48 (p. 126). Now the *atomic* weight of oxygen is 16. Clearly then, the molecule must contain 3 atoms, and ozone is correctly written O_3, ordinary oxygen being O_2.

But as far back as 1866, long before pure ozone had been obtained, Soret showed by a very ingenious method that the molecule of ozone was triatomic. He used two flasks, A and B, with long graduated necks. They were of the same volume (230 c.c.), and each was filled to the mark P or Q with ozonised air from the same sample (so that the percentage of ozone would be the same in each). The mouths of the flasks dipped into water.

Into A he introduced turpentine, which absorbs ozone. The water rose from P to X.

---

[1] In this equation and the next it has been convenient to assume that ozone is represented by O_3. The evidence for this will be given in the next paragraph.

The flask B was heated so as to turn the ozone into oxygen. After cooling to the original temperature, it was found that the water had been pushed down to Y, and *if the contraction in A was v c.c., the expansion in B was $v/2$ c.c.* (e.g. in one of his experiments the contraction in A was 6·9 c.c. and the expansion in B was 3·45 c.c.).

Now the contraction in A evidently gives the volume of ozone present in the sample, and this is the same in each, since the samples are similar. Thus the volume of ozone is v c.c., and when turned into oxygen this expands by $\frac{1}{2}v$ c.c., i.e. volume of oxygen $= v + \frac{1}{2}v = 1\frac{1}{2}v$ c.c.

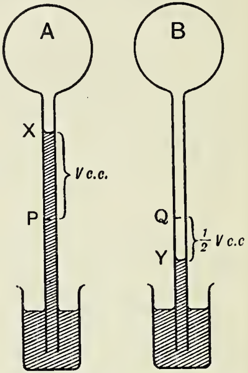

FIG. 14/2
Soret's experiment

Suppose v c.c. of ozone contains x molecules.

$\therefore$ v c.c. of oxygen contains x molecules (AVOGADRO).

$\therefore$ $1\frac{1}{2}v$ c.c. of oxygen contains $1\frac{1}{2}x$ molecules.

Thus instead of

'v c.c. of ozone becomes $1\frac{1}{2}v$ c.c. of oxygen,'

we may write

x molecules of ozone become $1\frac{1}{2}x$ molecules of oxygen.

$\therefore$ 1 molecule of ozone becomes $1\frac{1}{2}$ molecules of oxygen. But $1\frac{1}{2}$ molecules of oxygen contain 3 atoms (for 1 molecule contains 2 atoms).

$\therefore$ 1 molecule of ozone contains 3 atoms.

Soret was evidently much interested in the subject of ozone, for two years later he determined its constitution in another way, to which you will find a reference on p. 141, question 6.

Allotropy. In oxygen and ozone we have an example of the fact that the same element may show very different properties. This peculiarity (*phenomenon* is the proper word) is known as ***allotropy***—ozone is said to be an *allotropic form*, or *allotropic modification*, of oxygen. It will be clear from what has been said that the difference between the two is traceable to a difference in the molecules, though the atoms composing these are alike. As we continue our studies we shall come across a number of other examples of allotropy.

Uses. In Chapter 19 we shall see that 'organic matter' always contains carbon and usually hydrogen. Decaying organic matter, by serving as food for disease germs, may be injurious to health. It is easily destroyed, however, by burning, a process which turns the carbon and hydrogen into carbon dioxide and water. In this way complex molecules of injurious compounds are converted into harmless substances. We see the process at work when a gardener is burning garden refuse.

It is not always possible to *burn* organic matter, but the same purpose is served if we bring it into contact with a powerful oxidising agent. Hence ozone is sometimes used, for instance, in sterilising drinking-water. Among the water companies which employ this method may be mentioned those of Colne Valley, Maidstone and South Staffordshire. Of the water supply of Paris, about half (amounting in 1956 to some 65 million gallons per day) is dealt with in this way, the rest being treated by the cheaper method of chlorination (p. 258). Treatment by ozone gives excellent results, but is rather costly unless a very cheap source of electric power is available.

Ozone in the Atmosphere. G. M. Dobson, F.R.S., working at Oxford, showed some years ago that there is ozone in the atmosphere at a mean height of about 15 miles above sea-level. The amount is not large. At atmospheric pressure it would constitute a layer about $\frac{1}{8}$ inch thick.

It is doubtful if there is anything in the popular idea that there is a larger amount of ozone by the sea than inland. The amount present is in any case far too minute to be smelt, and the pleasant sarcasm of W. W. Jacobs (in *Sunwich Port*) is not far wide of the mark—'an honest, seafaring smell, compounded of tar, rope, and fish, known to the educated of Sunwich as ozone.'

HYDROGEN PEROXIDE

Preparation. A dilute solution of hydrogen peroxide, H_2O_2, is easily prepared in the laboratory by the action of dilute sulphuric acid on barium peroxide, the temperature being kept as low as possible:—

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$$

The solution of hydrogen peroxide may be decanted off, or filtered, from the precipitated sulphate.

Properties. Pure hydrogen peroxide is a colourless, syrupy liquid of sp. gr. 1·46. It blisters the skin. The dilute solution has an unpleasant metallic taste.

Its outstanding property is that it readily decomposes into water and oxygen, and it is therefore a powerful oxidising agent. Thus

(i) When a dilute solution is heated, oxygen is evolved:—

$$2H_2O_2 = 2H_2O + O_2$$

(ii) Lead sulphide is oxidised to lead sulphate (hence restoration of oil paintings, p. 475):—

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O$$

(to carry out the experiment, a piece of filter-paper is dipped in lead acetate solution and blackened by exposure to hydrogen sulphide. A few drops of hydrogen peroxide solution are then allowed to fall on the blackened paper, which is quickly turned white).

(iii) Iodine is liberated from potassium iodide,[1] and therefore starch-iodide paper is turned blue:—

$$2KI + H_2O_2 = 2KOH + I_2$$

(iv) Hydrogen sulphide, when passed into a solution of hydrogen peroxide, is oxidised to sulphur:—

$$H_2S + H_2O_2 = 2H_2O + S$$

Reaction with Permanganate. In the presence of sulphuric acid, hydrogen peroxide reacts with potassium permanganate. Oxygen is given off, half of it from the permanganate, half from the peroxide. The reaction is discussed on p. 491 in connection with volumetric analysis, and is the basis of a good method for finding the strength of a solution of hydrogen peroxide.

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[1] A case of oxidation, because potassium iodide loses the electropositive element potassium (see definition, p. 279).

Test for Hydrogen Peroxide. If a drop of potassium dichromate solution is added to a solution of hydrogen peroxide that has been acidified with sulphuric acid, an intense blue colour is produced. No doubt an oxidising action takes place, and it is believed that the blue substance is a perchromic acid, perhaps $HCrO_5$.

The blue compound is very unstable and soon disappears. Its solution in ether, however, is much more permanent, so it is usual to shake up the dichromate–peroxide mixture with ether, when the blue layer rises to the surface. In this form the test is an extremely sensitive one.

Uses. Owing to its oxidising action, hydrogen peroxide may be used for the removal of organic matter (p. 159), i.e. it is a disinfectant. It is often used as a mouth-wash, throat-gargle, etc., and a dentist uses it for cleansing the 'pulp-cavity' of a tooth when he has been obliged to kill the nerve. For such purposes it has the special advantage that as it does its work it is turned into perfectly harmless water. It is also used for bleaching substances that would be injured by the commoner bleaching agents—e.g. feathers, ivory, hair, teeth.

Questions

N.B. *See note in italics*, p. 132

1. Describe briefly how oxygen may be converted into ozone. *J.M.B. (part)*

2. A specimen of ozonised oxygen is equally divided between two flasks A and B. By absorption with turpentine it is found that A contains 8·4 c.c. of ozone. On heating B (to decompose the ozone contained in it) and afterwards cooling to the original temperature, an expansion of 4·2 c.c. is recorded. What conclusion can you draw with regard to the molecule of ozone? State clearly any assumptions contained in your argument.

3. Describe the properties of ozone.

On partly ozonising 100 c.c. of oxygen a decrease of volume of 10 c.c. resulted. What volume of ozone had been produced? The resulting gas was treated with excess of a solution of potassium iodide, when the following reaction took place:

$$O_3 + 2KI + H_2O = 2KOH + I_2 + O_2$$

Calculate (*a*) what volume of gas would remain, (*b*) what weight of iodine would be liberated, assuming the volumes to have been measured at N.T.P. *Camb.*

4. How would you prepare a dilute solution of hydrogen peroxide? Mention *two* uses of hydrogen peroxide, and give *one* distinctive test for this substance.

5. What volume of oxygen measured at N.T.P. could be obtained by boiling 20 gm. of a 5 per cent. solution of hydrogen peroxide?

6. Briefly describe the preparation and properties of an aqueous solution of hydrogen peroxide. From 50 c.c. of a solution of the peroxide, 112 c.c. of oxygen were obtained on boiling, the volume of the gas being measured at 18° C. and 750 mm. pressure. What was the amount of hydrogen peroxide in 1 litre of the original solution? *O.C.*

CHAPTER 15

CARBON

VERY pure carbon, known as *sugar charcoal*, may be obtained from sugar. The sugar is heated in a covered crucible, and soon becomes charred to a black mass. The latter contains a certain amount of hydrogen, which is removed by heating the mass in a stream of chlorine. (We shall see in Chapter 22 that chlorine readily combines with hydrogen.)

When pure sugar charcoal is heated in oxygen it burns, forming carbon dioxide, as we should expect. It is possible to absorb the whole of this carbon dioxide and weigh it, and careful experiment shows that from 1 gm. of pure charcoal we obtain 3·67 gm. of carbon dioxide. This fact is of such importance in connection with the study of carbon that we give a short description of the experiment by which it may be proved.

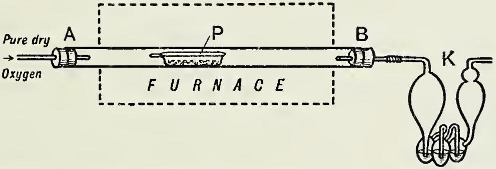

FIG. 15/1. Weighing the carbon dioxide formed by the combustion of carbon

The tube, AB, contains a porcelain boat, P, in which is a quantity of pure sugar charcoal. The tube is strongly heated by several bunsens, or, better still, by means of a muffle furnace. A slow stream of oxygen (from a cylinder), after being carefully dried and otherwise purified, passes over the charcoal. The latter burns as the oxygen passes over it, and the carbon dioxide produced is absorbed by potash bulbs, K, which contain a strong solution of caustic potash, a substance which eagerly combines with carbon dioxide.

Even sugar charcoal contains a trace of ash, i.e. it is not absolutely pure carbon. However, the difference between the weight of the porcelain boat (and contents) *after* the experiment and its weight *before* the experiment gives the weight of charcoal actually converted into carbon dioxide. The weight of this carbon dioxide is evidently equal to the increase in the weight of the potash bulbs.

Suppose, for instance, that 2·88 gm. of carbon had been burnt, and that the increase in the weight of the potash bulbs was 10·56 gm. We then have

2·88 gm. of carbon gives 10·56 gm. of carbon dioxide.[1]

$\therefore$ 1 ,, ,, ,, $\frac{10{\cdot}56}{2{\cdot}88} = 3{\cdot}67$ gm. ,,

To secure a really accurate result it is necessary to take certain precautions which have not been mentioned here. For instance, a quantity of copper oxide is placed between P and B to make sure that there shall be no carbon monoxide among the gases which pass on to the potash bulbs (carbon monoxide would react with heated copper oxide thus: $CO + CuO = CO_2 + Cu$).

We shall see presently that there are certain substances which really consist of carbon, and yet nobody would think so from their appearance. If after purification one of these substances gives 3·67 gm. of carbon dioxide per gram of substance oxidised, we know that we are dealing with carbon.

Wood charcoal is made by heating wood out of contact with the air. You may have made some accidentally at home when drying sticks in the oven and allowing them to get overheated. In the laboratory we can easily make a small specimen by putting some pieces of wood on an iron tray or in an evaporating dish, covering them with sand to keep out the air, and then heating.

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[1] It is convenient to notice that from this experiment we can obtain

(i) the equivalent of carbon. Thus with the numbers given, 2·88 gm. of carbon combines with 7·68 gm. of oxygen.

$\therefore$ 8 gm. of oxygen combines with $\frac{2{\cdot}88}{7{\cdot}68} \times 8 = 3{\cdot}00$, i.e. the equivalent of carbon is 3·00.

(ii) the percentage composition (by weight) of carbon dioxide. The percentage of carbon is $\frac{2{\cdot}88}{10{\cdot}56} \times 100 = 27{\cdot}3$, that of oxygen being $100 - 27{\cdot}3 = 72{\cdot}7$.

If the 'combustion tube' experiment described above is carried out with wood charcoal we find that

(i) a large quantity of non-combustible ash remains behind in the porcelain boat, but

(ii) for each gram of substance that *has* burnt away, 3·67 gm. of carbon dioxide is absorbed in the bulbs.

A fair conclusion from these observations is that though wood charcoal contains much carbon, it is not *pure* carbon. Similar remarks apply to coal, coke, anthracite, soot, lamp-black, animal charcoal and gas-carbon. These substances are often described as amorphous (i.e. non-crystalline) carbon. By modern methods, however, involving the use of X-rays, it has been found that their carbon constituent—for most of them contain a fair proportion of impurity—really consists of sub-microscopic crystals of graphite, a substance we shall be studying presently. 'Sub-microscopic' means, of course, 'Too small to be seen with a microscope.'

Charcoal has a curious power of adsorbing[1] gases. This is easily shown by collecting a test-tube of ammonia gas over mercury and putting a small piece of charcoal just under the mouth of the test-tube. The charcoal quickly floats to the top and the mercury soon begins to rise in the tube, showing that the gas is being adsorbed. This property has been turned to practical use in many ways. During the World War (1939–45), for instance, the gas masks issued both to civilians and soldiers contained a perforated canister of charcoal, made from wood or coal and afterwards 'activated,' i.e. treated in such a way as greatly to increase its power of adsorption. The usual method of treatment is to heat it in an electrical retort, out of contact with air, to a temperature of about 1100° C.

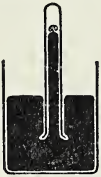

FIG. 15/2
Charcoal adsorbs gases

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[1] This word is preferred to *ab*sorbing because it is believed that the action takes place at the *surface* of the carbon—a surface which, in the case of a highly porous substance, may be of enormous extent.

Activated carbon has found many peace-time uses. It is employed for removing the excess of chlorine, after this gas has been used for sterilising drinking-water (p. 258), and for removing the vapours of solvents employed in various industries (rubber, artificial silk, etc.). It is also used for removing the colouring matter from certain solutions—crude sugar, for instance. In this case the substance adsorbed consists, not of a gas, but of extremely small particles of a solid material dispersed in a solution.

To go back to ordinary wood charcoal, we may note another useful property—that it does not readily undergo change at ordinary temperatures. For this reason a builder often chars the surface of the lower part of a post which he is putting in the ground.

Other varieties of so-called amorphous carbon are coke, anthracite, lampblack and animal charcoal. Coke is largely used in the great smelting industries, besides being employed as a domestic fuel. Lampblack has a great variety of uses. It is the chief constituent of black shoe-polish, and, worked up with boiled linseed oil, it gives us printer's ink and black paint. Another use is in connection with motor-car tyres, the lifetime of which is greatly lengthened by incorporating lampblack with the rubber. Animal charcoal, like the activated carbon already mentioned, is used for removing the colouring matter from solutions of crude sugar, etc. This property may be conveniently illustrated in the laboratory by adding a little ink to a quantity of water, warming for a few minutes with freshly heated animal charcoal and then filtering. The filtrate is practically colourless. Litmus solution may be used instead of ink.

Graphite differs from the substances hitherto mentioned in that its crystals are of appreciable size and not merely of sub-microscopic dimensions. It was formerly mined at Borrowdale in Cumberland, but these deposits have long since been worked out, and at the present time the best graphite is obtained from Madagascar and Ceylon.

At Niagara Falls large quantities of graphite are now made artificially by the *Acheson process*, which consists in strongly heating petroleum coke, mixed with a little sand and pitch, for about thirty hours in an electric furnace, the necessary energy being supplied by the waterfall. Acheson graphite is of a very high degree of purity, usually containing upwards of 99·8 per cent. of carbon. It is very soft and free from grit. With water containing a little tannin it forms a *colloidal suspension*, i.e. the suspended particles are so fine that they do not settle. This suspension is known as *aquadag*. A suspension in oil, *oildag*, can also be prepared (dag, d-a-g, =deflocculated Acheson graphite).

On account of its extreme softness, graphite (or one of its colloidal suspensions) can often be used as a lubricant where oil would be unsuitable, e.g. where very high temperatures are likely to develop, or where there is much dust. Because it is a good conductor of electricity it is sometimes used to form an extremely thin coating on conveyor belting, which can then be readily earthed. This prevents the building up of static charges on the belting, from which fires have sometimes resulted. The ironwork of stoves is often protected by being coated with graphite ('blacklead'). Here we are making use of the fact that graphite is not easily oxidised.

Blacklead pencils are made by mixing graphite with a plastic clay and squirting the mixture to form thin rods. For this purpose natural graphite (not 'Acheson') is always used. A modern use of graphite is as a 'moderator' in the atomic pile (p. 511). For this purpose it is important to employ graphite of the highest possible degree of purity.

Diamond is obviously a very different substance from graphite, but it resembles it in one important respect. When 1 gm. of the substance is burnt in a stream of oxygen it yields 3·67 gm. of carbon dioxide and nothing else. It is therefore a form of carbon. Before proceeding further, let us notice a few of the contrasts between the substances we are considering.

Diamond is colourless and transparent, while graphite is black and opaque. Diamond on account of its hardness—it is the hardest substance known—is used for cutting glass, while graphite on account of its softness is used, as we have seen, for making pencils and for lubricating machinery. Diamond has a relative density of $3\frac{1}{2}$, graphite of $2\frac{1}{2}$. From the point of view of chemical distinction, a most important point is that diamond and graphite differ completely in crystalline form.

In diamond and graphite in fact we have another example of an element existing in different *allotropic forms*—the previous example being that of ordinary oxygen and ozone. In the latter case it was possible to show that the difference is due to a different arrangement of the atoms, the molecule of oxygen containing two atoms and the molecule of ozone three. It was comparatively easy to do this because oxygen and ozone are gases, and it was only necessary to find their densities relative to hydrogen.

Evidently this method cannot be applied in the case of graphite and diamond, but as already mentioned, what is known as 'X-ray analysis' has made it possible to find how the atoms are arranged relatively to one another. It has been shown, for instance, that the atoms of graphite are arranged to form regular hexagons, multitudes of which are joined together in one plane as suggested by fig. 15/3. Parallel planes so formed would slip over one another, and no doubt this is connected with the lubricating properties of graphite.

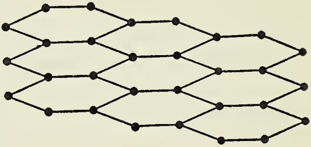


Fig. 15/3

Atoms in the diamond are also arranged with perfect regularity, but the pattern is more complicated, and the atoms are not in one plane. This makes 'slipping' impossible. From a study of the atomic pattern it is possible to account for the quality of extreme hardness, but we will not pursue the subject here.

This question of allotropic forms is a very interesting but rather puzzling one. We can obtain a very fair illustration from the theatre. An actor may be Julius Cæsar in one play, Hamlet in another and Shylock in a third, but he is always the same man really. Some of the chemical elements are very fond of the game of 'making up,' and carbon is one of the most successful of them.

Leaving diamond and graphite for the moment, what of the other substances we have mentioned—sugar charcoal, anthracite, lampblack, gas carbon and the rest? Are they also allotropic forms?

Some chemists recognise only the two forms diamond and graphite, on the grounds that sugar charcoal, etc., have been found to consist of sub-microscopic crystals of graphite. But these substances (sugar charcoal, etc.) differ so obviously from graphite in their general properties that it seems reasonable to regard them as a separate allotropic form, and so it is more usual to recognise *three* such forms, diamond, graphite and 'amorphous' carbon. It really would be better, however, that some other word, such as 'micro-crystalline,' should be substituted for 'amorphous.' Meanwhile, we can get over the difficulty fairly well by putting the word in inverted commas, implying that we know very well that it does not mean quite what it says.

There remains the difficulty that there are many differences between the members of the 'amorphous' group. Sugar charcoal, for instance, differs very much from gas carbon. In some cases we can account for the differences. The adsorptive power of coconut charcoal and animal charcoal, for example, is due to the cellular structure of the materials from which they are prepared. In other cases the properties may be greatly influenced by the presence of impurities, just as the presence of less than 1 per cent. of impurity is known to affect very greatly the properties of copper, aluminium and other metals. It may be that further knowledge will cause us to recognise other allotropic forms, but for the present we regard all varieties of carbon that are not obviously diamond or graphite as constituting only one allotropic form. There is no harm, however, in our saying that wood charcoal and gas carbon, for instance, are different *varieties* of this one allotropic form, the so-called 'amorphous carbon.'

Conversion of One Form into Another. If pig iron formed by smelting is slowly cooled, ordinary graphite crystallises out. This is, of course, derived from the coke, and so sub-microscopic crystals have been converted into much larger ones. We have in fact converted one allotropic form, 'amorphous' carbon, into another, graphite. Another change of form may be brought about by heating a diamond, using the electric arc, to a temperature approaching 2000° C. in the absence of air. It swells up and changes into graphite.

Naturally, however, men have been far more interested in the problem of obtaining diamonds from one of the other forms of carbon, and many attempts have been made. It appears that diamonds are formed in Nature by the action of a high temperature and enormous pressure, and chemists have sought to make diamonds in the laboratory by imitating these conditions.

As far back as 1880 J. B. Hannay at Glasgow, starting with carbon obtained from paraffin, obtained twelve tiny crystals which he believed to be small diamonds. (Incidentally his laboratory was nearly wrecked by the explosion of one of his reaction tubes.) These were kept at South Kensington, and sixty years later scientists using modern methods of testing found that all but one of these crystals were indeed diamonds. In February 1955 very small diamonds were made at the General Electric Research laboratory at Schenectady, New York. The pressure employed in this case was over 50,000 atmospheres. Moissan (1893) thought he had succeeded in making diamonds from charcoal, but it is now generally believed that he was mistaken.

Nobody so far has come anywhere near to making diamonds of 'gem' size. The products might perhaps be used in tools for cutting and polishing, but at present the cost of production would be far too great.

Questions

1. Sketch and label, *without* further description, an apparatus for burning a known weight of carbon in air to form carbon dioxide only, and absorbing the gas so that it can be weighed. *Oxf.* (*part*)

2. In an experiment such as is illustrated by fig. 15/1 it was found that 2·37 gm. of pure sugar charcoal yielded 8·69 gm. of carbon dioxide. What value does this give for the equivalent of carbon?

3. In a determination of the equivalent weight of carbon 0·74 gm. of the element was burnt in a current of oxygen, the products of combustion were passed over heated copper oxide, and the resulting carbon dioxide was absorbed in potash bulbs. The increase in weight of the potash bulbs was 2·69 gm. Calculate to two places of decimals the equivalent weight of carbon. What was the object of using copper oxide in this experiment? *Camb.*

4. 6 gm. of sugar charcoal, heated in a stream of oxygen as indicated in fig. 15/1, was found to yield 22·00 gm. of carbon dioxide. 1 gm. of diamond yielded 3·67 gm., while 3 gm. of graphite yielded 9·90 gm. of carbon dioxide, but left in the porcelain boat a residue of 0·30 gm. of incombustible ash.

Show that an important conclusion can be drawn from the above results.

5. Explain what is meant by the term *allotropy*, using the allotropic forms of carbon to illustrate your answer.

How can it be shown that the allotropic forms of carbon are different forms of the same element? *Camb.* (*part*)

CHAPTER 16

CARBON DIOXIDE

In Chapter 8, when discussing the composition of the atmosphere, we saw that carbon dioxide gets into the air in a number of ways. It is produced during the breathing of animals and also during the combustion of all common fuels—coal, wood, paraffin, etc.—because these fuels contain carbon. Large quantities of carbon dioxide must also pass into the air during the decay of vegetable matter.

Carbon dioxide is also produced in the growth of the yeast plant (though this is certainly not one of the important sources of atmospheric carbon dioxide). Possibly you have seen a little yeast put into a solution of sugar. After a few hours the liquid begins to ferment, and the gas given off consists of carbon dioxide, while alcohol is formed in the liquid. On this principle is based the brewing of beer and other alcoholic drinks.

In a similar way carbon dioxide is produced during the making of bread (yeast, sugar and water all being present). The bubbles of gas are produced inside the dough, and puff it out, making it light and porous.

Preparation. The most convenient way to prepare a number of jars of the gas is by the action of dilute hydrochloric acid on marble chips. It may be collected either by displacing air upwards (fig. 16/1) or by displacement of water (fig. 16/2). The equation is

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

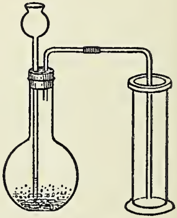


Fig. 16/1. Displacing air upwards

N.B. Examiners are very fond of asking how this or that gas is prepared *pure* and *dry*.

The method of purifying a gas depends, of course, on what particular impurities are likely to be present. In the case under discussion the carbon dioxide would probably contain a little hydrogen chloride gas, and this would be removed by passing it through a wash-bottle containing a little water, or, better still, a solution of sodium bicarbonate. The equation for the reaction which takes place when hydrogen chloride passes through this solution is given on p. 179.

A gas is usually *dried* by passing it through one or more U-tubes containing calcium chloride, or through bottles containing concentrated sulphuric acid (e.g. see fig. 22/2).

Avoid the very common mistake of first explaining how to dry the gas *and then collecting it over water.* A dry gas must be collected either by displacement of air or over mercury.

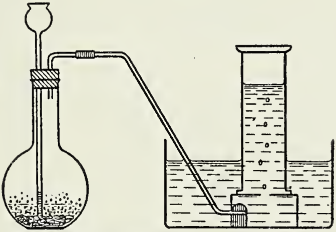


FIG. 16/2. Preparation of carbon dioxide

Properties. Carbon dioxide is colourless and has a faint, sweetish smell and taste, rather pleasantly suggestive of soda-water. It dissolves in water somewhat easily. In fact, if it were *much* more soluble than it is, it would not be possible to collect it over water. The solution contains a weak acid known as carbonic acid, H_2CO_3 $(H_2O+CO_2=H_2CO_3)$. Assuming the formula to be CO_2, we see that the molecular weight is $12+32=44$, and therefore the density relative to hydrogen is 22 (p. 126). The density of air relative to hydrogen is 14·4, so that carbon dioxide is about half as heavy again as an equal volume of air. It is rather easily liquefied.

A small quantity of *solid* carbon dioxide, sometimes called 'carbonic acid snow,' may easily be obtained as follows:

Take one of the 'sparklet' bulbs used in making soda-water. Place over this a piece of black velvet, say 9 inches by 4, through the middle of which the point of a 3-inch nail has been pushed. The point of the nail is placed on the 'nose' of the bulb and then knocked in with a hammer. Carbon dioxide rushes out and is immediately frozen by the cooling effect caused by its own expansion, the 'snow' collecting on the velvet.

In 1928 'dry ice'—solid compressed carbon dioxide—began to be manufactured in England, and by 1947 the annual output was not far short of 20,000 tons. It is used as a refrigerant.

Carbon dioxide is largely used in making 'fizzy' mineral waters. The simplest of these is soda-water, mentioned above, made by dissolving large quantities of the gas in water, under pressure. When the pressure is released the excess gas bubbles out freely. By the addition of sugar, flavouring and colouring mater, all sorts of 'soft drinks' may be prepared.

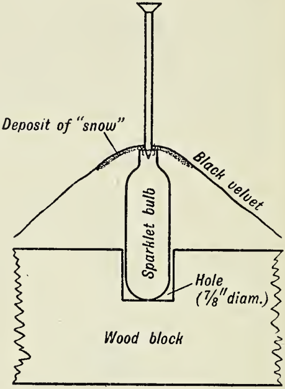


FIG. 16/3. Production of solid carbon dioxide

Another use is in the manufacture of fire extinguishers. One type consists of a strong metal vessel containing a solution of sodium carbonate, inside which is a glass tube or bottle of sulphuric acid. On striking the knob of the extinguisher, an attached rod causes the bottle to be broken. Carbon dioxide is produced in great quantity by the action of the acid on the carbonate, and a jet consisting of a frothy mixture of gas and liquid rushes out of the nozzle.

We must now consider the chemical properties of carbon dioxide. It neither burns nor supports combustion. It is identified by the fact that it turns lime-water milky:—

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

How do we know that the gas obtained by the action of acid on marble chips is really an oxide of carbon? The answer is that the gas so obtained resembles in every way the gas obtained by burning carbon in oxygen. It has, for instance, the same density, the same curious action on lime-water and the same effect on litmus solution, which is turned to a not very decided red. Lastly, we can easily prove that the gas certainly contains carbon, and probably oxygen. Some magnesium ribbon is put in a deflagrating spoon and ignited. When it is well alight it is plunged into a jar of the gas. Although the latter is, generally speaking, a non-supporter of combustion, the magnesium continues to burn. The white fumes in the jar and the white residue on the spoon look very like magnesium *oxide*. If that is the case, the gas must contain *oxygen*. By adding a little hydrochloric acid to the jar and shaking up we can get rid of the white fumes. At the bottom of the jar we notice some black specks. The latter should be separated from the liquid by filtration, washed and transferred to a crucible. On strongly heating the latter, the black specks completely disappear—a very fair test for *carbon*.

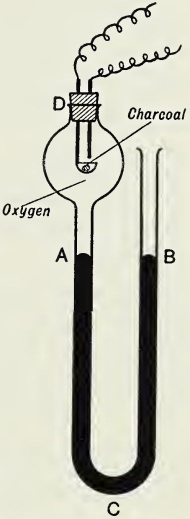


FIG. 16/4. Composition of carbon dioxide

Formula of Carbon Dioxide. It can be shown that the molecule of carbon dioxide contains

(*a*) one molecule, i.e. two atoms, of oxygen, and

(*b*) one atom of carbon.

To prove the first statement we use the apparatus of fig. 16/4. The part ACB contains mercury, while the space above A is filled with oxygen. The stopper D carries two stout copper wires, one of which ends in a spoon. The gap between the spoon and the other copper wire is filled with a thin spiral of iron wire. Inside the spiral, and partly supported by the spoon, is a small piece of charcoal. On passing an electric current the charcoal is heated and soon takes fire in the oxygen. The mercury at A is pushed down at first owing to expansion of the enclosed gas, but when the latter has cooled down to its original temperature, the mercury is found to return exactly to its original position. Thus from a certain volume of oxygen we have obtained an exactly equal volume of carbon dioxide, i.e.

(i) 1 vol. of carbon dioxide contains 1 vol. of oxygen.

Suppose '1 volume' of carbon dioxide contains n molecules,

$\therefore$ 1 vol. of oxygen also contains n molecules (AVOGADRO).

Instead of (i) we may therefore write

n molecules of carbon dioxide contain n molecules of oxygen.

$\therefore$ 1 molecule of carbon dioxide contains 1 molecule of oxygen.

But 1 molecule of oxygen contains 2 atoms.

$\therefore$ 1 molecule of carbon dioxide contains 2 atoms of oxygen.

The formula is therefore C_xO_2, where x remains to be found.

To determine x, we find the density of carbon dioxide relative to hydrogen—a comparatively simple experiment. It turns out to be 22, so that the molecular weight is 44 (p. 126). From 44 subtract 32 (the weight of two atoms of oxygen). The remainder, 12, is the weight of the carbon present, and 12 is the weight of *one* atom of carbon. Thus $x = 1$, and the required formula is CO_2.

Carbonic Acid and Carbonates. We have seen that carbonic acid is a very weak acid formed by the action of carbon dioxide on water ($CO_2 + H_2O = H_2CO_3$). When carbon dioxide is dissolved in water only a very small portion of it actually *combines*—most of it simply dissolves. When you drink a glass of soda-water you are *not* drinking carbonic acid, but a solution of carbon dioxide containing a minute quantity of the acid.

Carbonic acid would not be of much importance but for the fact that it gives rise to the *carbonates*, formed when the hydrogen (in H_2CO_3) is replaced by a metal. On p. 42 we saw that sodium (Na), potassium (K) and silver (Ag) are all univalent, *i.e.* one atom of each of these metals replaces one atom of hydrogen, so that two atoms will replace two atoms, and so on. Thus sodium carbonate is Na_2CO_3, potassium carbonate is K_2CO_3 and silver carbonate (not often met with) is Ag_2CO_3. The group ammonium, NH_4, is also univalent, so that ammonium carbonate is $(NH_4)_2CO_3$. Make sure that you know this little list by heart—sodium, potassium, silver, ammonium.

Almost all the other metals which you will meet with in elementary chemistry are divalent (the chief exception is iron, which is sometimes trivalent). Thus calcium (Ca) replaces two atoms of hydrogen, whence the formula for calcium carbonate is $CaCO_3$. Similarly we have magnesium carbonate $MgCO_3$, lead carbonate $PbCO_3$ and so on.

Since one atom of sodium replaces one of hydrogen, there seems no reason why from carbonic acid, H_2CO_3, we should not derive a compound of the formula $NaHCO_3$. Such a compound actually exists. It is the well-known 'baking soda,' its chemical name being sodium hydrogen carbonate, or sodium bicarbonate. Similarly we have potassium bicarbonate, $KHCO_3$.

Considering 'bicarbonate,' HCO_3, as a group, it is clear that it must be univalent, since it combines with one atom of sodium, etc. Now we sometimes find this group combined with divalent metals such as calcium. In such a case clearly *two* groups would be required, and so calcium bicarbonate would be $Ca(HCO_3)_2$ (cf. calcium chloride, $CaCl_2$).

How Carbonates Are Made. Carbonates, of course, are salts, and therefore we might expect to make them by the methods described on p. 153. Do *not*, however, use such phrases as 'Add carbonic acid to a metal, or to its oxide or hydroxide.' This would reasonably be understood in the sense of *pouring* (as one pours sulphuric acid, etc.), and the amount of carbonic acid that can be added in this way is small in the extreme. We can 'add carbonic acid' to a substance only by suspending or dissolving the substance in water and passing a stream of carbon dioxide through. In this way carbonic acid is re-formed as fast as it is used up.

The methods in practical use for making carbonates are

(1) Passing carbon dioxide through a solution or suspension of the hydroxide. We have a well-known example in the production of calcium carbonate from lime-water.

If carbon dioxide is passed through a solution of sodium hydroxide, first the carbonate is produced and then the bicarbonate (both are soluble):—

$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$
$$Na_2CO_3 + H_2O + CO_2 = 2NaHCO_3$$

A solution of sodium hydroxide absorbs carbon dioxide so readily that it is often used when we wish to remove this gas from others with which it may be mixed.

(2) Double decomposition. Thus calcium *chloride* is soluble in water and so is sodium *carbonate*. On adding one solution to the other, calcium carbonate is precipitated:—

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$$

This method can be used for the preparation of practically any carbonate except those of sodium, potassium and ammonium, which are soluble in water.

Bicarbonates. You know that if you keep on passing carbon dioxide into lime-water after it has turned milky, it goes clear again after a while. This is because the insoluble calcium carbonate has been turned into soluble bicarbonate:—

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2$$

You cannot obtain the solid bicarbonate by evaporating to dryness, because as soon as you begin to heat, the bicarbonate decomposes, carbon dioxide being given off and calcium carbonate precipitated.

Sodium bicarbonate also can be obtained by passing carbon dioxide through a solution of the carbonate (equation has been given above). This bicarbonate is easily decomposed by heat, but not so easily as calcium bicarbonate, so it is possible to obtain the substance in the solid condition (the experiment is described on p. 420). As already mentioned, it is commonly known as baking soda.

Action of Heat and Acids on Carbonates, etc. We have already seen that the action of heat on bicarbonates is to decompose them—sometimes with extreme ease—into carbonates. If you pour boiling water on baking soda you can see by the effervescence that decomposition is taking place:—

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

We can easily distinguish sodium carbonate from sodium bicarbonate by the fact that, on gently heating, the bicarbonate yields carbon dioxide while the carbonate is unchanged. When sodium bicarbonate is used for baking, the chemical change mentioned above causes carbon dioxide to be produced inside the dough, thus making it 'light' as already explained. It has the further advantage (from the confectioner's point of view) of turning it to a light yellow colour, as though eggs had been used on a generous scale. Unfortunately the chemical change leaves in the cake a residue of sodium carbonate (i.e. washing soda minus its water of crystallisation), and if the quantity is considerable, the taste is thoroughly unpleasant.[1]

Carbonates when heated usually decompose, the basic oxide being left behind while carbon dioxide is evolved (e.g. $CaCO_3 = CaO + CO_2$). The temperature required varies a great deal, but is usually rather high. *The carbonates of sodium and potassium do not decompose at all, however high the temperature.*

The action of acids on carbonates and bicarbonates is to decompose them, carbon dioxide being evolved. We had an example in the case of marble chips and hydrochloric acid for the preparation of carbon dioxide. Two other cases are represented by the following equations:—

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2$$

$$NaHCO_3 + HCl = NaCl + H_2O + CO_2$$

---

[1] The writer vividly recalls being one of a party which sat down to a farm-house tea after a long country ramble. There was a large dish of rock buns of most inviting 'eggy' colour, but scarcely anybody got further than a mouthful or two. The taste of sodium carbonate was very marked.

In baking powder the constituents are sodium bicarbonate and (usually) tartaric acid. The latter is a solid, and no action takes place until it gradually dissolves in the water present in the moist dough. Seidlitz powders, 'health salts,' etc., are similar mixtures, citric acid (the acid of lemons) being sometimes used instead of tartaric. The reason why one is instructed to 'use a dry spoon' will be obvious.

Hardness of Water. Water is often met with which does not readily give a lather with soap. It is then said to be *hard.* When hard water is evaporated to dryness there is always a residue consisting of some calcium[1] salt, usually the carbonate or sulphate. Now soap is the sodium salt of a fatty acid known as stearic acid, i.e. soap is sodium stearate.[2] Hence when hard water containing, say, calcium sulphate is brought into contact with soap solution, a double decomposition takes place:

$$\begin{matrix}\text{Sodium}\\\text{stearate}\end{matrix} + \begin{matrix}\text{Calcium}\\\text{sulphate}\end{matrix} = \begin{matrix}\text{Sodium}\\\text{sulphate}\end{matrix} + \begin{matrix}\text{Calcium}\\\text{stearate}\end{matrix}$$

Calcium stearate is insoluble and forms a white precipitate. You can see it floating about on the surface after you have been washing your hands in hard water.

It is clear that after a time all the calcium salt originally dissolved in the water will have been precipitated as calcium stearate. From that moment the soap will play its ordinary part of producing a lather.

Hard water, then, brings about waste of soap,[3] converting it into useless calcium stearate. We must, therefore, consider two questions:—

(1) How does water become hard?

(2) How can it be softened?

The answer to the first question is that the water must have flowed over land containing calcium compounds. Much the commonest one is calcium carbonate (a great part of the Pennine Chain, for instance, consists of limestone, the North and South Downs consist of chalk and so on). Now for all practical purposes calcium carbonate is insoluble in water—that is the reason for the milkiness produced when carbon dioxide is passed into lime-water. We have already seen, however, that in the presence of carbon dioxide and water insoluble calcium carbonate is turned into soluble calcium bicarbonate:—

---

[1] In some districts a magnesium salt, or there may be both. In what follows, what is said about calcium also applies roughly to magnesium.

[2] Sodium oleate and sodium palmitate are usually present as well. They have an action very similar to that of the stearate.

[3] It has been calculated that in London alone the value of the soap wasted in this way is more than £250,000 a year.

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2$$

This reaction is constantly taking place in a district containing chalk or limestone. Rain containing carbon dioxide that has been dissolved out of the air falls on the limestone; calcium bicarbonate is produced and passes into solution.

To soften such water all we have to do is to *boil* it, when the reaction just described is reversed:—

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2$$

Carbon dioxide escapes, calcium carbonate settles to the bottom of the kettle, saucepan, etc., and the water is soft.

Hardness which can be removed by boiling, i.e. *hardness due to the presence of calcium bicarbonate in solution, is said to be* ***temporary.***

Temporary hardness is sometimes removed by *Clark's process*, usually applied on the large scale, e.g. to the entire water supply of a town. By careful analysis, the amount of calcium bicarbonate in solution is ascertained, and the exact amount of milk of lime is added to precipitate all the calcium in accordance with the equation[1]

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$$

If too much milk of lime is added, the water will still be hard—harder than before perhaps. The reason is, of course, that we still have a calcium compound in solution, this time calcium hydroxide.

---

[1] It has been shown that bacteria present in the water are also carried down with the fine precipitate of calcium carbonate. Thus the water is not only softened but, if previously infected, is made safe for drinking.

So much for temporary hardness. If the hardness is due to the presence of some calcium compound other than the bicarbonate—calcium sulphate for instance—boiling will make no difference. *Hardness which cannot be removed by boiling is said to be **permanent**.*

Permanent hardness may be removed by the addition of sodium carbonate, washing soda ($Na_2CO_3.10H_2O$) being usually employed. This causes the calcium to be precipitated as carbonate[1]:—

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$$

A modern method of softening water is known as the *Permutit process.* A cylinder containing 'permutit' is installed, the ordinary house supply of hard water is made to pass through it, and soft water is drawn off.[2] Let us see how it works.

Permutit, which looks like a coarse sand, is a complex substance which we may describe as sodium alumino-silicate. We will represent it as $Na\overline{P}$. If hard water (containing, say, calcium sulphate) flows over this, we get

$$2Na\overline{P} + CaSO_4 = Na_2SO_4 + Ca\overline{P}_2$$

Thus calcium is removed from the water, being left behind in the cylinder as calcium alumino-silicate. After a while the substance ceases to act properly because so much of the sodium compound has been turned into the calcium compound. To restore it, a solution of common salt is poured in and left overnight. We get

$$Ca\overline{P}_2 + 2NaCl = CaCl_2 + 2Na\overline{P}$$

Thus the sodium alumino-silicate is re-formed, and the process of water-softening can be continued.

Comparison of Hardness. We can make a rough comparison of the hardness of several samples of water by means of a 1 per cent. solution of Castile soap. We take equal quantities, say 25 c.c., of each sample, and find what volume of the soap solution has to be added to each in order to produce a 'permanent lather' (i.e. one which remains for two minutes).

---

[1] Hence, in applying Clark's process, it is usual now to add the calculated quantity of sodium carbonate as well as milk of lime.

[2] An experiment illustrating this is described on p. 62 of the author's *School Course of Practical Chemistry* (Bell).

Similarly we could find how much of the hardness of a given sample was temporary, and how much was permanent. Suppose 25 c.c. of the sample takes 35 c.c. of soap solution. Now boil a measured quantity of the sample to remove temporary hardness, and add just enough distilled water to make up for loss by evaporation. Take 25 c.c. of the product, and find how much soap solution is required now. Suppose the amount is 5 c.c. Thus the *permanent* hardness is represented by the number 5, while the *total* hardness is represented by the number 35. The difference, 30, represents the temporary hardness. In this case, then, six-sevenths of the hardness is temporary and one-seventh is permanent.

Hard water for such experiments as these is easily prepared in the laboratory. For temporary hardness, we pass carbon dioxide through lime-water until it has become first milky and then clear again. This gives us, of course, a solution of calcium bicarbonate. To illustrate permanent hardness we may take a saturated solution of calcium sulphate (it is only very slightly soluble) or we may use a solution of calcium chloride of about 1 per cent. strength.

Questions

N.B. *See note in italics*, p. 132

1. Mention *three* cases in which one meets with carbon dioxide in processes of daily life.

2. Describe how you would prepare and collect a few jars of carbon dioxide, starting with marble. Give *three* uses of the gas.

How would you verify that carbon dioxide contains its own volume of oxygen?

What changes take place when (*a*) burning magnesium is lowered into a jar of carbon dioxide, (*b*) carbon dioxide is passed into a cold concentrated solution of sodium carbonate? *W.J.*

3. A piece of calcspar ($CaCO_3$) was placed in 200 c.c. of dilute hydrochloric acid and warmed until no more dissolved. The original weight of the calcspar was 4·5 gm.; after the reaction it weighed 2·0 gm. Calculate the concentration of the acid in grams of hydrochloric acid per litre.

What volume of gas at N.T.P. will be evolved during the reaction? (1 gm. of hydrogen occupies 11·2 litres at N.T.P.) *O.C.*

4. Describe the experiments you would perform to obtain a sample of carbon from calcium carbonate.

Explain the formation of hard water and of stalactites in a limestone district. *Scot.L.C.*

5. Starting with a piece of chalk, how would you prepare (*a*) quicklime; (*b*) slaked lime; (*c*) lime-water; (*d*) a jar of carbon dioxide?

How does carbon dioxide react with (*e*) magnesium; (*f*) carbon; and (*g*) sodium carbonate? State what conditions are required for reaction in each case. *Dur.*

6. How would you prepare and collect carbon dioxide from washing-soda crystals?

What volume of carbon dioxide would be evolved from 10 gm. of the above crystalline decahydrate at 10° C. and 740 mm. pressure?

How would you obtain baking soda from washing soda? *Brist.*

7. Calculate the volume of gas collected at 15° C. and 740 mm. pressure, and the weight of the solid residue obtained, on heating 10 gm. of sodium bicarbonate. *Lond.* (*part*)

8. How would you prepare and collect a sample of pure water from tap-water?

Describe the tests you would make to determine whether a sample of tap-water contains permanent hardness. If it does, how would you find whether the hardness is due to dissolved sulphate?

Starting from distilled water and being provided with a supply of carbon dioxide and quicklime, how would you make a sample of temporarily hard water? What is the chemical reaction that occurs when soap solution is added gradually to temporarily hard water, and what change is visible? *Lond.*

9. Describe and explain what you would see when: (*a*) carbon dioxide is passed for a long time through lime-water; (*b*) some of the product of (*a*) is boiled; (*c*) sodium carbonate solution is added to the product of (*a*); (*d*) lime-water is added to the product of (*a*). *O.C.*

CHAPTER 17

CARBON MONOXIDE

Carbon monoxide is sometimes seen burning with a blue flame on the top of a good red glowing fire—of a watchman's bucket fire in the street for instance. It is formed in this way. At the bottom and edges of the fire the glowing carbon (coal or coke) is in contact with air, and can therefore take up all the oxygen it wants. The carbon therefore becomes carbon dioxide ($C + O_2 = CO_2$), and this is drawn through the middle of the fire. Here there is carbon eager to combine with oxygen, but there is no oxygen to be had, except what is present in the carbon dioxide which is passing through. The latter is therefore *reduced* while the carbon in the fire is oxidised

$$CO_2 + C = 2CO$$

At the top of the fire there is a full supply of oxygen available, and the carbon monoxide will combine with this, forming carbon dioxide ($2CO + O_2 = 2CO_2$). It is this combination which is accompanied by the blue flame of which we have spoken.

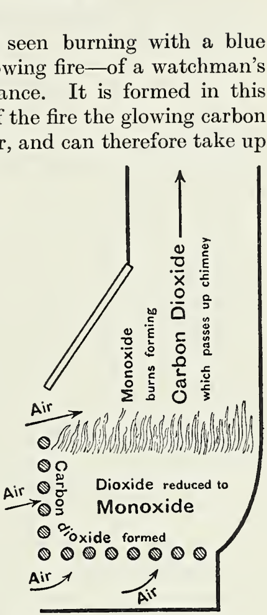


Fig. 17/1. How carbon monoxide is produced in a fire

Producer-gas and Water-gas. In many works where they desire to have a fuel which is cleaner and more easily regulated than coal or coke, special stoves are made in which carbon monoxide is formed as described above, but is not given a chance to turn into dioxide because the stove is closed in at the top. The carbon monoxide, mixed, of course, with atmospheric nitrogen, is led away by a pipe and can be burnt as required. The mixture is known as *producer-gas.* It contains 25 or 30 per cent. of carbon monoxide, but its value as a fuel is impaired by the fact that it contains a large proportion, 60 per cent. or so, of non-combustible nitrogen.

If steam instead of air is passed over white-hot coke, the oxygen of the steam combines with carbon, forming carbon monoxide, and hydrogen is set free:—

$$H_2O + C = CO + H_2$$

The mixture, known as *water-gas*, contains about 50 per cent. of hydrogen and 40 per cent. of carbon monoxide. As *both* of these are combustible gases, one would expect water-gas to be much more effective as a source of heat then producer-gas; in fact it usually has well over twice the 'calorific value.'

As the steam passes over the white-hot coke, the temperature of the latter soon falls, until by and by the action would cease altogether. Before this stage is reached, however, the current of steam is shut off and a current of air is turned on. This causes producer-gas to be formed as described above, and in the process the coke becomes hotter and hotter, until after a while the air can be turned off and replaced by steam, water-gas being formed once more. Thus producer-gas and water-gas are formed alternately, the former with rise of temperature, the latter with fall of temperature. The gases are usually collected in separate gas-holders. We see that when water-gas is produced by passing steam over coke, heat is *absorbed.* Such a reaction is said to be ***endothermic.*** When heat is given out in the course of a chemical reaction, the latter is said to be ***exothermic.*** When air is passed over coke, for instance, we have an exothermic reaction.

Laboratory Production. The fact that carbon monoxide is formed when carbon dioxide is passed over heated carbon can easily be shown in the laboratory. An iron tube, AB, packed with charcoal, is passed through a muffle furnace, and carbon dioxide from the flask F (containing marble chips and hydrochloric acid) passes over it. The carbon dioxide is *reduced* to carbon monoxide in the way already described, and the monoxide may be collected over water in the jar J. C, containing caustic soda, is to remove unchanged dioxide.

A more convenient method of obtaining the gas is shown in fig. 17/3. The flask A contains a handful of crystals of oxalic acid. This is covered with concentrated sulphuric acid and heated. A mixture of equal volumes of carbon monoxide and dioxide is produced, but by passing the gas through the two Woulff bottles B and C, containing a strong solution of caustic soda, the carbon dioxide is removed, and the monoxide then collects in the jar D.

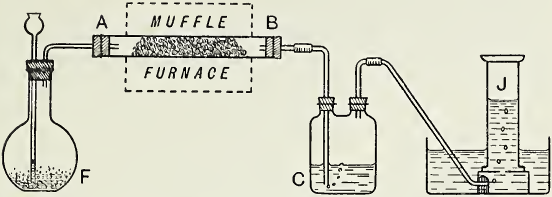


FIG. 17/2. Carbon dioxide reduced to monoxide

Oxalic acid has the formula $H_2C_2O_4$, and the chemical change is represented by the equation

$$H_2C_2O_4 = H_2O + CO + CO_2$$

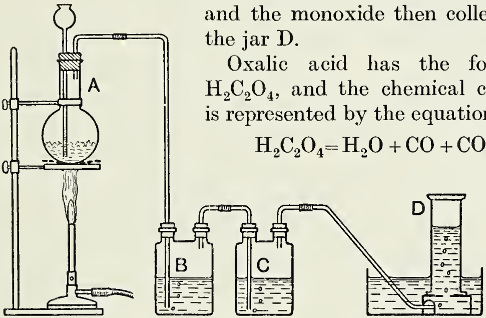


FIG. 17/3. Carbon monoxide from oxalic acid

Sulphuric acid acts by withdrawing the elements of water.

N.B. (1) Avoid saying 'by withdrawing *water*'; oxalic acid does not contain water, though it contains the elements from which this substance is made.

(2) Students often say that the sulphuric acid acts as a catalyst (no doubt because it does not appear in the equation).

A catalyst, however, would be unchanged at the end of the process, and would therefore be capable of further action. In this case, on the other hand, the sulphuric acid is diluted, and soon becomes incapable of withdrawing the elements of water from further supplies of oxalic acid.

Preparation from Formic Acid. We may use formic acid instead of oxalic acid. It is more expensive, but there is the advantage that no carbon dioxide is produced. The apparatus is shown in fig. 17/4. The sulphuric acid is first heated to 80° or so, and the formic acid, a colourless liquid, is run in from a tap funnel, a few drops at a time.

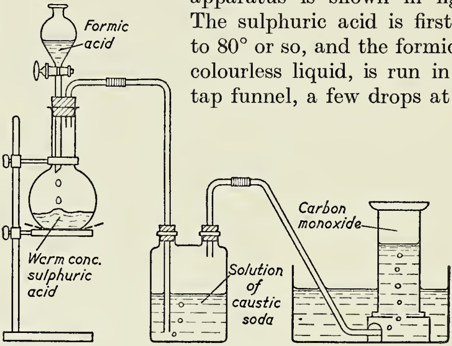


FIG. 17/4

As in the preparation from oxalic acid, the sulphuric acid acts by withdrawing the elements of water.

$$H \cdot COOH = H_2O + CO$$

Formic acid boils at 100°, and some of the vapour passes over with the gas, but is removed by the dilute caustic soda in the wash-bottle.

Poisonous Nature of Carbon Monoxide. Carbon monoxide is a very poisonous gas, and it is worth while to understand the reason. The blood contains a substance called hæmoglobin, and this readily combines with oxygen breathed in by the lungs, forming an unstable compound called oxyhæmoglobin. As the blood passes round the body, this substance decomposes, giving the tissues the oxygen they need and being once more converted into hæmoglobin. It is now, of course, in a condition to form oxy-hæmoglobin afresh, and to repeat its work.

Now hæmoglobin will combine with carbon monoxide far more readily than it will with oxygen, forming a compound called carboxy-hæmoglobin. This is incapable of giving the tissues the oxygen they need, and death soon results. As small a proportion as 1 volume in 40,000 of air will produce a violent headache if breathed for long. One volume in 8000 will produce death in half an hour, and 1 in 100 in about two minutes. The gas is, of course, all the more dangerous from the fact that it has no smell.

Carbon monoxide is often produced as the result of imperfect combustion. Thus it may be given off from a defective bathroom geyser or from the exhaust pipe of a motor-car. We often read in the newspapers of fatal accidents due to the gas having been formed in such circumstances.

General Properties. Carbon monoxide has neither colour nor smell. It is a very little lighter than air and is practically insoluble in water. It has no effect on litmus or lime-water. It burns with a beautiful blue flame, with the production of carbon dioxide.

We could obtain carbon from this carbon dioxide (by burning magnesium in it, as described on p. 175), and this would have been present in the original monoxide. Thus we have a means of showing that carbon monoxide contains carbon.

It is readily absorbed by a solution of cuprous chloride (Cu_2Cl_2) in hydrochloric acid, and we may make use of this fact to remove carbon monoxide from a mixture of that gas with hydrogen.

In the presence of sunlight it unites directly with an equal volume of chlorine, forming a gas known as phosgene, or carbonyl chloride, $COCl_2$.

Owing to the fact that it readily combines with more oxygen (forming the dioxide), we are not surprised to find that it acts as a powerful *reducing agent*, i.e. a substance that takes away oxygen from other substances. Thus if copper oxide is heated in a stream of the gas, it is reduced to copper

$$CuO + CO = Cu + CO_2$$

Many other oxides, those of lead and iron for instance, are in a similar way reduced to the corresponding metal.

Composition by Weight. The reaction with copper oxide, mentioned above, may be used to help us in finding the composition of carbon monoxide by weight (*gravimetric* composition). Dry carbon monoxide is passed over a tube containing copper oxide, the total weight of which is known, and the carbon dioxide produced is absorbed in weighed potash bulbs (cf. K in fig. 15/1, p. 163). Suppose the copper oxide loses 1·00 gm. in weight, while the potash bulbs gain 2·75 gm.

Now it may be found by experiment that carbon dioxide contains 27·3% of carbon (by weight) and 72·7% of oxygen (footnote, p. 164), and working from this, we find that the 2·75 gm. of carbon dioxide contains 0·75 gm. of carbon and 2·00 gm. of oxygen.

The 0·75 gm. of carbon must have come from the carbon monoxide. Of the 2 gm. of oxygen, only 1 gm. came from the copper oxide.

∴ the other 1 gm. must have come from the carbon monoxide, i.e. it was combined with 0·75 gm. of carbon.

Hence, composition of carbon monoxide is—carbon 0·75 gm., oxygen 1·00 gm., which works out to 42·9% carbon and 57·1% oxygen.

Formula of Carbon Monoxide. To show that carbon monoxide is represented by the formula CO, a measured quantity of the gas is mixed with excess of oxygen in a eudiometer, over mercury. The mixture is sparked, and the volume of carbon dioxide produced is found by introducing a strong solution of caustic soda into the space over the mercury, and observing how much the latter rises. (The caustic soda could be introduced by means of a bent pipette, but other methods are used in actual practice.)

We now know

(*a*) The original volume of carbon monoxide, say v c.c.[1]

(*b*) The volume of oxygen that was added.

(*c*) The volume of oxygen left over (i.e. the volume *not* absorbed by the caustic soda).

(*d*) The volume of carbon dioxide produced.

---

[1] Allowance would have to be made in every case for the length of the mercury column in the tube, the various volumes concerned all being reduced to the same pressure.

Subtracting (*c*) from (*b*) we get the volume of oxygen required to combine with v c.c. of carbon monoxide. This turns out to be $\frac{1}{2}v$ c.c., while the volume of carbon dioxide is found to be v c.c. Thus

v c.c. monoxide + $\frac{1}{2}v$ c.c. oxygen give v c.c. dioxide.

Suppose the $\frac{1}{2}v$ c.c. of oxygen contains n molecules,

∴ v c.c. of monoxide contains $2n$ molecules, and so does the v c.c. of dioxide (AVOGADRO).

∴ $2n$ mols. monoxide + n mols. oxygen give $2n$ mols dioxide.

Dividing by $2n$

1 mol. monoxide + $\frac{1}{2}$ mol. oxygen = 1 mol. dioxide.

$$\begin{aligned} \therefore 1 \text{ mol. monoxide} &= 1 \text{ mol. dioxide} - \tfrac{1}{2} \text{ mol. oxygen} \\ &= CO_2 \qquad\qquad - \tfrac{1}{2}O_2 \\ &= CO \end{aligned}$$

Volume of Carbon Monoxide in a Mixture. In the last experiment we *knew* the volumes of carbon monoxide and of oxygen and were able to *find* the formula. Conversely, if the formula is taken for granted, we can find the volume of carbon monoxide, as in the following.

Example 1. *A mixture of carbon monoxide and nitrogen, having a volume of* 65 *c.c., was mixed with an equal volume of oxygen, and sparked. The volume was now* 105 *c.c., but after absorption with caustic soda this was reduced to* 55 *c.c. Find the volume of carbon monoxide and of nitrogen in the original mixture.*

The equation which represents the reaction is

$$\begin{array}{ccccc} 2CO & + & O_2 & = & 2CO_2 \\ \textit{2 mols.} & & \textit{1 mol.} & & \textit{2 mols.} \end{array}$$

This shows that the carbon monoxide and dioxide are equal as regards number of molecules, therefore they are equal as regards volume (AVOGADRO). Now the volume of carbon dioxide is 50 c.c., because this is the volume absorbed by caustic soda.

∴ vol. of carbon monoxide also = ***50 c.c.***
∴ vol. of nitrogen = 65 − 50 = ***15 c.c.***

From the information given, we can work out the answer in another way. On sparking, there was a contraction of

$$65 + 65 - 105 = 25 \text{ c.c.}$$

Now the above equation shows that if the total volume before sparking is 3 vols. (2 vols. monoxide + 1 vol. oxygen), the volume afterwards is 2 vols., so that contraction = 1 vol.

∴ vol. of monoxide = *twice* amount of contraction

$$= 2 \times 25 \text{ c.c.}$$
$$= \mathbf{50 \text{ c.c.}} \text{ as before.}$$

Example 2. *A mixture of carbon monoxide and hydrogen has a volume of* 30 *c.c., and* 25 *c.c. of oxygen is added. After sparking, the volume is reduced to* 28 *c.c. Find the percentage composition of the original mixture.*

The required equations are

$$2CO + O_2 = 2CO_2$$
$$2H_2 + O_2 = 2H_2O$$

Let vol. of carbon monoxide = x c.c.

∴ „ „ hydrogen = $30 - x$ c.c.

On sparking, contraction due to x c.c. monoxide would be $\frac{1}{2}x$ (see previous example).

And contraction due to $30 - x$ c.c. hydrogen would be $1\frac{1}{2}(30 - x)$. (For the equation shows that 2 vols. hydrogen and 1 vol. oxygen *practically disappear altogether*, since the water formed, being liquid, is of negligible volume. Thus the contraction, 3 vols., $= 1\frac{1}{2}$ times vol. of hydrogen.)

∴ total contraction $= \frac{1}{2}x + 1\frac{1}{2}(30 - x) = 27$.

(For original vol. was $30 + 25$, and final vol. = 28.)

Solving the equation, we get $x = 18$.

∴ vol. of carbon monoxide = 18 c.c.,

and „ „ hydrogen = $30 - 18 = 12$ c.c.

Expressed as a percentage, this gives ***carbon monoxide 60 per cent., hydrogen 40 per cent.***

Uses of Carbon Monoxide. Carbon monoxide has a number of uses. We have already referred to its value as a fuel in the mixture known as producer-gas. Since 1895 it has been used to an ever-increasing extent in what is called the 'Mond process' for the extraction of nickel. More recently, chemists have discovered a method for making an important liquid known as methyl alcohol from water-gas (carbon monoxide and hydrogen). Methyl alcohol has the formula CH_3OH, and the action looks simple enough on paper

$$CO + 2H_2 = CH_3OH$$

In practice it is necessary to use a suitable catalyst (copper mixed with zinc oxide). Methyl alcohol is at present largely used in the manufacture of dyes and perfumes, and one of these days may be used for the driving of motor-cars and aeroplanes.

A great number of most useful organic substances contain only carbon, hydrogen and oxygen. The difficulty is to know how to make these elements combine, but the results obtained so far, using carbon monoxide, hydrogen, air and a catalytic agent have been very promising indeed. There is no doubt that great discoveries lie ahead.

Questions

N.B. *See note in italics*, p. 132

1. Account for the blue flames seen over a clear coke fire.

2. How would you prepare a sample of carbon monoxide, free from carbon dioxide, in the laboratory?

What are the reactions of carbon monoxide with (*a*) oxygen, (*b*) hæmoglobin of the blood?

How would you show the presence of carbon in carbon monoxide? *Dur.*

3. What weight of crystallised oxalic acid, $H_2C_2O_4.2H_2O$ would be required for the production of 10 gm. of carbon monoxide? What volume would be occupied by this gas (i) at N.T.P., (ii) at 14° C. and 75 mm. pressure?

4. 10 c.c. of carbon monoxide is exploded with 20 c.c. of oxygen in a eudiometer, over mercury. What volume of gas is left, and what is its composition? (All volumes are measured at the same temperature and pressure.) *Lond.*

5. A gaseous mixture is believed to consist of carbon dioxide, carbon monoxide and hydrogen. Describe experiments by which it could be ascertained if each of these gases is actually present.

How could the proportion of *one* of these gases in such a mixture be determined? *Lond.*

6. Describe the manufacture of (*a*) producer-gas, (*b*) water-gas. Explain why it is not possible to use a continuous process for the preparation of water-gas. Which of these gases is more efficient as a fuel, and why is this so? How would you demonstrate that both producer-gas and water-gas contain carbon monoxide? *Camb.*

7. Write the equation for the combustion of water-gas ($CO + H_2$) in air ($4N_2 + O_2$). Given that the gram molecular weights of all gases occupy equal volumes when measured at equal temperatures and pressures, write down the volume of air required to burn 2 litres of water-gas and the volumes of the products, all measurements being made at atmospheric pressure and 150° C.

Oxf. (*part*)

8. Write an account of the manufacture of water-gas. State two uses to which this gas is put.

50 c.c. of water-gas were exploded with 50 c.c. of oxygen. The volume after the explosion was 50 c.c. On introducing sodium hydroxide the volume was further reduced to 25 c.c. Explain the changes in volume, calculate the percentage composition of the water-gas and show that excess of oxygen was used for the explosion. *Scot.L.C.*

9. Say what you can of the uses of carbon monoxide.

CHAPTER 18

CERTAIN HYDROCARBONS

A HYDROCARBON is a compound containing hydrogen and carbon *only*. Do not confuse the word with 'carbohydrate.' 'Hydrate' suggests water, and a carbohydrate is a compound containing carbon, hydrogen *and oxygen*, the last two elements being present in the same proportions as they occur in water. Thus cane sugar, $C_{12}H_{22}O_{11}$, is a carbohydrate.

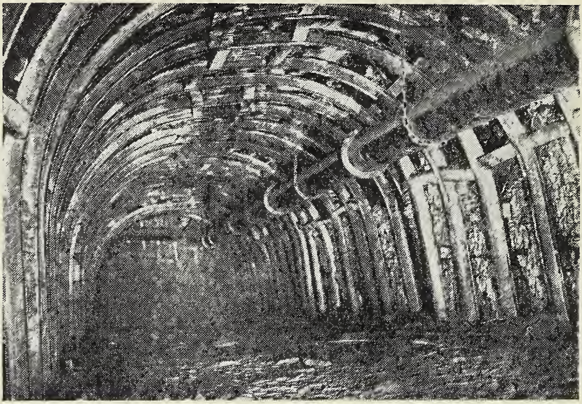
The hydrocarbons are extremely numerous and important, but in this chapter we shall study only three of them, viz. methane (CH_4), ethylene (C_2H_4) and acetylene (C_2H_2). We shall have occasion however to refer briefly to several others.

Methane constitutes, roughly, 30 per cent. of ordinary coal-gas. It has sometimes been called 'marsh-gas,' because it often rises to the surface as bubbles when the bottom of a marshy pool is stirred. In this case it has been formed by the decay of organic matter.

A somewhat related fact is that it is formed by the decomposition of sewage, and sometimes the gas so produced is collected and used as a fuel (its calorific value is actually higher than that of coal-gas). In Birmingham, for instance, it is burnt in gas-engines at the sewage-works, so providing power for pumping and other purposes.

The 'fire-damp' so dreaded by the miner on account of its explosive qualities also consists largely of methane. Nowadays in the case of a number of mines—about twenty in Great Britain—arrangements for securing 'methane drainage' have been made. The illustration shows the removal of methane through a 14-inch pipe ($3\frac{1}{2}$ miles long) at the Haig Colliery in Cumberland. The reduced 'gassiness' of the mine has enabled production to be stepped up by 55 per cent. (to 1700 tons per day). The piped-off gas is used as a fuel, chiefly for operating machinery used in the mine. In this way it is saving about 300 tons of washed coal per week.

In the laboratory methane is usually made by heating a mixture of sodium acetate and soda-lime (the latter is made by slaking quicklime with a strong solution of caustic soda instead



By courtesy of National Coal Board

Methane drainage, Haig Colliery

of with water). The mixture may be heated in a hard-glass test-tube, but a copper flask is better. The gas is collected over water:—

$$CH_3 . \boxed{COONa + NaO}H = Na_2CO_3 + CH_4$$

Sodium acetate

Ethylene, C_2H_4, is produced by heating alcohol with sulphuric acid at a temperature of 165° C. The final result is that the alcohol loses the elements of water:—

$$C_2H_6O = H_2O + C_2H_4$$

Acetylene is produced when a bunsen burner 'strikes back,' though most of the unpleasant smell is due to the presence of other hydrocarbons. It is present to a very small extent in coal-gas.

It is prepared in the laboratory from the same materials as are used in the acetylene bicycle-lamp—calcium carbide and water—and is collected over water:—

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

N.B. A common mistake is to write $CaC_2 + H_2O = CaO + C_2H_2$.

A sensitive test for acetylene is furnished by its reaction with a solution of cuprous chloride (Cu_2Cl_2) in ammonia. It forms a red precipitate of cuprous acetylide, Cu_2C_2.

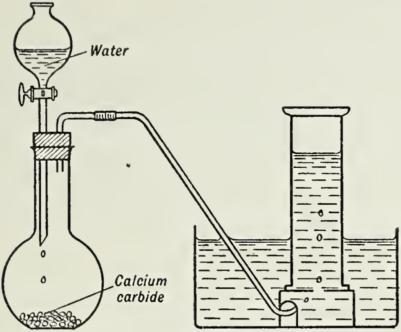


FIG. 18/1. Preparation of acetylene

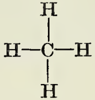
Properties. The three hydrocarbons mentioned above are all colourless gases. Methane is the least and acetylene the most soluble of the three, but in no case is the gas too soluble to be collected over water. All burn readily, with the production of carbon dioxide and water:—

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$
$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$$
$$2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O$$

The flame of methane is non-luminous, that of ethylene is distinctly luminous and that of acetylene is brilliantly luminous and smoky. In short, so far as these three gases are concerned, the higher the proportion of carbon, the more luminous is the flame. We shall understand this point better after our study of Flame in Chapter 20.

All three gases react with chlorine (and other halogens), but here there is a marked contrast between methane, on the one hand, and ethylene and acetylene, on the other. Thus methane forms compounds in which one or more atoms of chlorine are *substituted* for an equal number of atoms of hydrogen—compounds having the formulæ CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 being formed ($CHCl_3$ stands for the well-known chloroform, and CCl_4 for carbon tetrachloride, used as a fire-extinguisher—'Pyrene'—and as a cleaning agent). Ethylene, however, *adds on* chlorine (and other halogens), forming compounds with the formulæ $C_2H_4Cl_2$, $C_2H_4Br_2$, etc. Similarly, starting from acetylene, we obtain $C_2H_2Cl_2$, $C_2H_2Cl_4$, $C_2H_2Br_2$, etc. We express these facts by saying that methane forms *substitution* products, while ethylene and acetylene form *addition* (or *additive*) products.

It is not very hard to understand this difference of behaviour. The carbon atom is tetravalent, and in methane all the valencies are engaged thus:—



$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

Hence carbon can take on chlorine only by first dropping an equivalent of hydrogen.

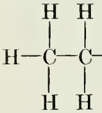
In ethylene and acetylene, however, the carbon atoms have valencies in reserve, so to speak. Thus the molecule of acetylene might be represented as $H-C\equiv C-H$. When chlorine is presented, these reserve valencies readily attach themselves to it. A compound such as ethylene or acetylene is said to be *unsaturated*, while one such as methane is said to be *saturated*. It will be clear that while a saturated compound can form only substitution products, an unsaturated compound can also form addition products. Thus ethylene and acetylene are far more chemically active than methane, simply because they are unsaturated.

One of the addition reactions just discussed is of special importance because of a great industry to which it has given rise. In 1899 Professor Sabatier of Toulouse showed that if a mixture of acetylene and hydrogen is passed over finely divided nickel at the ordinary temperature, the saturated compound ethane (C_2H_6) is produced

$$C_2H_2 + 2H_2 = C_2H_6$$

He argued that very likely other unsaturated compounds could be made to take up hydrogen in a similar way, and the final outcome of his experiments was a process by which comparatively valueless oils (unsaturated compounds) could be turned into hard fats (saturated) of great use in the soap-making and margarine industries. (See Introduction, p. 4.)

C_2H_6, not C_2H_8. We have just referred to 'the saturated compound ethane (C_2H_6),' and knowing that the carbon atom has four valency bonds, the student perhaps expected the formula C_2H_8. Actually, one of the bonds from each carbon atom is exercised *on the other carbon atom*, so we have the formula



$$H-\underset{\displaystyle H}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}-\underset{\displaystyle H}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}-H$$

, or C_2H_6.

Proof of Formula. To return to methane. When it is exploded with oxygen in a suitable tube, carbon dioxide and water are formed. The volume of carbon dioxide is readily found by absorbing the gas with caustic potash. The gas still remaining consists of unused oxygen. Subtracting this from the volume of oxygen originally taken, we get the volume which was required for the combustion of the methane. On examining the results it is found that

1 vol. methane + 2 vols. oxygen = 1 vol. carbon dioxide + water.

Suppose 1 vol. of methane contains x molecules,

$\therefore$ 2 vols of oxygen contain $2x$ molecules (AVOGADRO),

and 1 vol. of carbon dioxide contains x molecules,

$\therefore$ x mols. methane + $2x$ mols. oxygen = x mols. carbon dioxide + water.

Dividing by x,

1 mol. methane + 2 mols. oxygen = 1 mol. carbon dioxide + water.

Now the molecule of carbon dioxide contains one atom of carbon, which must have come from the methane, i.e. the molecule of methane contains one atom of carbon. Again, of the 2 molecules of oxygen, one was used up in forming CO_2. The other molecule must have been required to combine with the *hydrogen* in the molecule of methane. Therefore this hydrogen must have consisted of 4 atoms.

Hence the formula is CH_4. This is confirmed by the fact that the density relative to hydrogen is 8, giving a molecular weight of 16, as would be required by the formula CH_4.

When a similar experiment is carried out with ethylene the result obtained is that

1 vol. ethylene reacts with 3 vols. oxygen, giving 2 vols. carbon dioxide and some water.

It will be a good exercise for the student to show from this information that the formula must be C_2H_4.

The formula for acetylene could, of course, be obtained in the same sort of way.

Uses. It has already been mentioned that methane is an important constituent of coal-gas. The natural gas found in many parts of the world (mostly in connection with oil-wells) usually contains a large proportion of methane, sometimes as much as 98 per cent. It is often used as a source of power and light. In fact, in the United States about three-quarters of the gas used is natural gas, and it is conveyed by pipes over very great distances—in one case as much as 1840 miles (Texas to New York City).

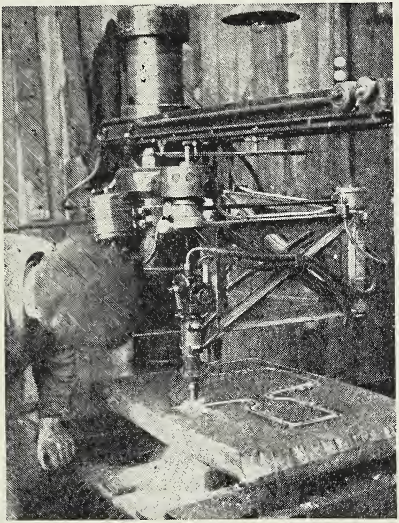
Ethylene is present to a small extent in coal-gas. As an anæsthetic, many doctors prefer it to ether.

As we saw in the chapter on Oxygen, the acetylene flame, fed with oxygen, is very largely used for cutting and welding.

The high temperature of the flame is partly due to the fact that acetylene is an *endothermic* compound, i.e. when it is formed from its elements heat is absorbed, and therefore when it is decomposed an equal amount of heat is given out. We can divide the burning of acetylene into two stages: (i) decomposition, (ii) oxidation of the carbon and hydrogen produced in (i). During *each* of these processes heat is given out.

Most compounds are exothermic, and if they are burned, heat is *absorbed* during the decomposition part of the process.

Acetylene is also a useful illuminant in cases where supplies of coal-gas or electricity are not available—houses in remote country districts, light-houses, buoys, etc.; and the acetylene bicycle-lamp was formerly in very general use. At one time acetylene was supplied in cylinders under high pressure, just as oxygen is to-day. It was found, however, that in certain circumstances disastrous explosions were apt to result, and it was forbidden by law to supply the gas in this form.



By courtesy of 'Machinery'

Cutting valve yokes with the oxy-acetylene flame

The method now adopted depends on the fact that acetylene is very soluble in a liquid called acetone, this solubility being proportional to the pressure in accordance with what is known as Henry's Law. As the pressure is released, the acetylene escapes, much as carbon dioxide escapes from a freshly opened bottle of mineral water.

The equation $2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O$ shows that for the complete combustion of one volume of acetylene, $2\frac{1}{2}$

volumes of oxygen are required, i.e. 12½ volumes of air, since only about one-fifth of the air consists of oxygen.

The burners first used gave unsatisfactory results because they failed to supply a sufficient volume of air, with the result that much free carbon was produced. The difficulty has been overcome by the use of a burner in which the gas issues through two (or more) very fine jets, arranged so as to suck in air somewhat on the principle of the bunsen burner.

Coal-gas. Owing to the fact that coal-gas contains a number of hydrocarbons, we have several times had occasion to refer to it. We will now give a brief account of the way in which it is prepared and purified.

It is prepared by heating coal in closed retorts,[1] the fuel used for heating being producer-gas (p. 185). The crude gas leaves the retorts by vertical *ascension pipes*, which finish by turning downwards into a closed trough of water known as the *hydraulic main*. This serves to remove some of the tar and ammonia, and it also acts as a water-seal, so that when a retort has to be opened, gas will not pass back into it.

The hot crude gas next passes through the *condenser*,[2] a series of iron pipes, usually water-cooled. Here much of the remaining tar vapour is condensed, and is collected in the tar-well. Above the tar is 'ammoniacal liquor' (water formed by condensation, with ammonia and other impurities dissolved in it).

Beyond the condenser is the *exhauster*—a rotary pump designed, on the one hand, by pressure, to drive the gas forward against the various resistances it has to meet, and on the other, by suction, to assist the removal of gas from the retorts.

The gas still contains some tar in the form of minute droplets showing as *tar fog*, which is removed by a *tar separator* (not shown in the figure). In one pattern a disc-shaped brush, revolving slowly, first passes through water in the lower half of the separator, after which the wet bristles make contact with the stream of gas in the upper portion, and the tar particles stick to the bristles.

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[1] A laboratory experiment illustrating the process is described on pp. 148–9 of the author's *School Course of Practical Chemistry* (Bell).

[2] Fig. 18/2 illustrates the broad principle, but the modern condenser usually consists of an iron tower traversed by a number of vertical iron pipes through which water passes 'in parallel.' The gas passes down the tower, between the cooled pipes.

The tar-free gas now passes through a *scrubber* or *washer*, the construction of which will be clear from the diagram. Here the remaining ammonia is dissolved out.

The chief remaining impurity is hydrogen sulphide. It is important to remove it, because if left in it would on burning produce sulphur dioxide (p. 307), with its strong smell of burning sulphur. The hydrogen sulphide is removed by passing it through *purifiers*—large iron boxes containing 'bog ore' (hydrated ferric oxide, i.e. Fe_2O_3 combined with one or more molecules of water. In the equations which follow these combined molecules are omitted for simplicity). The hydrogen sulphide turns the hydrated oxide into ferric sulphide:—

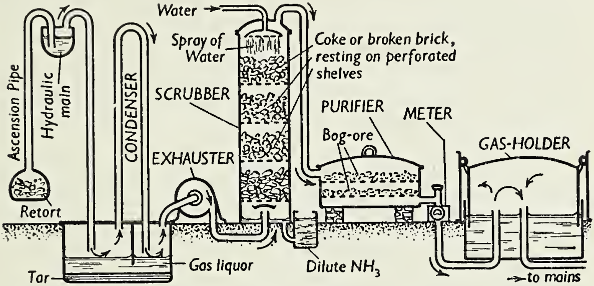

FIG. 18/2

$$Fe_2O_3 + 3H_2S = Fe_2S_3 + 3H_2O$$

After a while, so much of the oxide has been turned into sulphide that it ceases to be effective. The mixture is therefore removed from the purifier and exposed to the air, which causes it to be gradually 'revivified' (sometimes a current of air is blown through it, giving quicker results).[1]

$$[Fe_2S_3 + 3O = Fe_2O_3 + 3S] \qquad 2Fe_2S_3 + 3O_2 = 2Fe_2O_3 + 6S$$

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[1] In some works a little air is mixed with the gas as it enters the purifier, so that the sulphide may be revivified without the necessity for removal.

The revivified material (hydrated ferric oxide, but now containing some free sulphur) is returned to the purifier for a further spell of duty. After several such transfers the sulphur content will have increased to 50 or 60 per cent. by weight, and the mixture will be rather ineffective. It may then be sent off to the sulphuric works, where the sulphur can be burnt out of it, giving sulphur dioxide for use in the manufacture of acid. Some large gas-works have a sulphuric acid plant as part of their equipment.

After passing through the hydrated oxide, the purified gas goes through a large meter where it is measured, and thence to the gas-holder (commonly known by the not very suitable name of 'gasometer').

As coal-gas is a mixture, its composition may, of course, vary widely, but the following would be fairly typical: hydrogen 47 per cent., methane $23\frac{1}{2}$, carbon monoxide 14, unsaturated hydrocarbons (ethylene, etc.), 3, impurities (chiefly nitrogen, carbon dioxide and oxygen) $12\frac{1}{2}$.

In most modern plants the hot coke in the retorts is 'steamed,' causing the production of water-gas (hydrogen + carbon monoxide, p. 185). It is this operation which accounts for part of the 14 per cent. of carbon monoxide mentioned above.

It may be noted here that a ton of coal carbonised by modern methods would yield about 13,000 cu. ft. of coal-gas. About 13 cwt. of coal would be produced, of which say 3 cwt. would be used to make producer-gas for heating the retorts, leaving 10 cwt. to be sold.

'Ammoniacal liquor' has been mentioned, and when we come to study ammonia (p. 318) we shall see how this can be turned into a valuable fertilizer—ammonium sulphate. For this, sulphuric acid is required and, as we have said above, this is sometimes made in connection with the gas-works itself.

Besides the by-products already mentioned—coke and ammonium sulphate—our original ton of coal would yield about 10 gallons of tar, which serves as the raw material for an almost countless number of useful products.

Other Hydrocarbons. We cannot very well close our chapter on hydrocarbons without saying something about natural oil; for natural oil is a mixture of hydrocarbons—probably of thousands of them. It is found in many parts of the world, especially in U.S.A., Russia and the Middle East. Wells are sunk—some of them extremely deep—and the crude oil is usually run off in pipes to towns on the coast, often hundreds of miles away, to be refined. It is first washed with alkalis and sulphuric acid and then distilled. One or two rather unusual substances come over in the first fraction, but soon afterwards, at a temperature of about 50–60°, petrol distils off and is separately collected. It has to be redistilled and purified in various other ways before it is fit for use.

At higher temperatures 'paraffin oil' comes over, and later still a distillate from which paraffin and vaseline may be extracted, leaving a heavy oil suitable for lubrication. The residue in the retort consists of bitumen or asphalt.

We have only to think for a moment to realise what an important part is being played in our present-day civilisation by the hydrocarbons. Unlike coal, they can be used to operate an internal-combustion engine. Hence they are being used in ever-increasing quantities to drive our motor-cars, our aeroplanes and many of our most powerful ships.

Questions

N.B. *See note in italics,* p. 132

1. Describe the preparation and collection of dry methane in the laboratory. Why is methane called 'a saturated hydrocarbon'? 100 c.c. of a mixture of methane and hydrogen required 100 c.c. of oxygen (measured under the same conditions) for complete combustion. Find the composition of the mixture. *Brist.*

2. It was found that 10 c.c. of a gaseous compound of carbon and hydrogen required 20 c.c. of oxygen for complete combustion, and after combustion yielded 10 c.c. of carbon dioxide.

What is the compound? How would you prepare a specimen of it in the laboratory? *Brist.*

3. The gaseous hydrocarbon ethane has the molecular formula C_2H_6. Calculate (*a*) its relative density, (*b*) the volume occupied by 0·3 gm. of the gas at 17° C. and normal pressure, (*c*) the volume of air (containing one-fifth oxygen) necessary for the complete combustion of 60 c.c. of this gas.

Assume that 1 litre of hydrogen at N.T.P. weighs 0·09 gm.

(A balanced equation must be written.) *Lond.*

4. (i) What volume of acetylene measured at 10° C. and 76 cm. pressure, and (ii) what weight of slaked lime would be produced by adding excess of water to 32 gm. of calcium carbide?

5. 27 c.c of a mixture of methane and ethylene required 66 c.c. of oxygen for its combustion, and yielded 39 c.c. of carbon dioxide. From these data calculate the percentage composition (by volume) of the original mixture. *Camb.*

6. You are given gas-jars which are known to contain methane, ethylene or acetylene. Describe exactly how you would proceed to find out the nature of the contents of each jar (marks will not be given for a mere statement of the properties of the gases). *O.C. Alt.*

7. Compare the properties of acetylene with those of methane. What volume of hydrogen may be obtained from 100 c.c. of each of these gases? *Camb.*

8. Outline the process used for the manufacture of coal-gas. Name the other main products obtained, and describe how the gas is purified for domestic use. *Camb.* (*part*)

9. Name *three* inflammable gases which are present in coal-gas. State what reactions occur when each of these is burnt completely in air. *Camb.*

CHAPTER 19

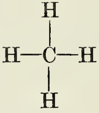
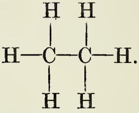
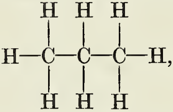
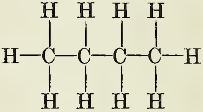
ORGANIC CHEMISTRY

You have no doubt heard the term *Organic Chemistry*, and wondered how this differs from the *Inorganic* that you are mainly studying. In this chapter we shall explain the meaning of the term, and consider a few organic compounds that are of outstanding importance in daily life. Further, we shall try to understand some of the problems that confront the organic chemist, and his method of solving them.

First, then, the meaning of the term. At one time it was firmly believed that many chemical compounds could be produced only in connection with animal or vegetable life. Sugar formed from beetroot and formic acid present in the body of the ant would be just two examples. Because (it was maintained) such substances could not be produced in the laboratory, but only by the action of living *organ*isms, they were regarded as *organic* compounds, and the study of them was known as *Organic* Chemistry.

But in 1828 the German chemist Wöhler was heating a solution of ammonium cyanate, NH_4CNO, a substance which can be made in the laboratory and is therefore 'inorganic.' To his astonishment the heated solution, on cooling, deposited crystals which he quickly recognised as the 'organic' compound urea (present in urine)—organic, according to the belief of that day, because it could be produced only by the action of the kidneys, as part of the life process. Soon, other organic substances were produced by 'inorganic' methods, and before long it was realised that the division between the two terms was a rather artificial one.

It was soon noticed, however, that substances hitherto thought to be produced only by the action of life contained the element *carbon*, and their number was so great that it was found convenient to retain the name, though not with the old meaning. To-day, organic chemistry means simply the chemistry of the compounds of carbon, while inorganic chemistry is the chemistry of all other compounds. At the present time, something like 30,000 inorganic compounds are known, but the number of known organic compounds is enormously greater, probably somewhere between half a million and a million; and the number is increasing by leaps and bounds. The question arises, Why should the number of carbon compounds so vastly outnumber those which do not contain carbon? We will deal with this question at once.

In the preceding chapter we saw that carbon was regarded as possessing four valency bonds, and that we could write methane as  $\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$ and ethane as  $\begin{array}{cccc} & H & H & \\ & | & | & \\ H- & C- & C- & H \\ & | & | & \\ & H & H & \end{array}$. We notice the beginning of a little *chain* of carbon atoms, —C—C—. But the chain can be longer. We have propane, C_3H_8,  $\begin{array}{ccccc} & H & H & H & \\ & | & | & | & \\ H- & C- & C- & C- & H \\ & | & | & | & \\ & H & H & H & \end{array}$, butane C_4H_{10},  $\begin{array}{cccccc} & H & H & H & H & \\ & | & | & | & | & \\ H- & C- & C- & C- & C- & H \\ & | & | & | & | & \\ & H & H & H & H & \end{array}$, and so on. These structural formulæ[1] are often expressed more concisely. The last one, for instance, would be written $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$, or even $CH_3[CH_2]_2CH_3$. There is a compound known in which as many as *sixty* carbon atoms are linked in a long chain. Its molecular formula is $C_{60}H_{122}$, and no doubt, given a good-sized piece of paper, you could write out its structural formula for yourself. Abbreviated, it would be $CH_3[CH_2]_{58}CH_3$.[2]

Other atoms besides carbon may form chains, but usually only very short ones. The structural formula of hydrogen peroxide, for instance, is probably H—O—O—H, where we have a chain of two oxygen atoms. Silicon forms longer ones, as we shall see in Chapter 33; but carbon far outdistances all other elements in this respect, and that is one of the chief reasons why its compounds are so very numerous.

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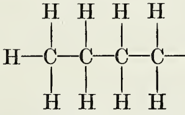
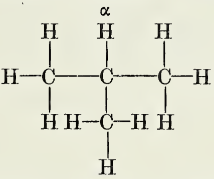
[1] Formulæ showing the *structure* of the molecule—the way in which the atoms composing it are linked up.

[2] The existence of hydrocarbons containing many atoms of carbon and of hydrogen is not in good accord with the law of Multiple Proportions. Consider, for instance, the two paraffins of formulæ $C_{19}H_{40}$ and $C_{20}H_{42}$. It can easily be shown that for a fixed weight of hydrogen, the weights of carbon in the two compounds are in the ratio 400 : 399. Not a very 'simple' one!

The compounds known to Dalton contained only *small* numbers of atoms (e.g. CO, CO_2), so he had no need to wrestle with complications such as we have just considered.

We said 'one of the chief reasons,' because there is another. If you write the structural formulæ of methane, CH_4, ethane, C_2H_6, and propane, C_3H_8 (already given on p. 208), and keep to what we will call 'the rules of the game,' you will find that each of these formulæ can be written in only one way. By the 'rules of the game' we mean that every carbon atom is to be given four bonds, every hydrogen atom one, and that each bond is to connect a carbon atom either to another carbon atom or to a hydrogen atom.

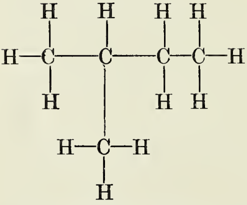
But now let us deal with the next compound in the series, butane, C_4H_{10}. We write at once  $\begin{array}{ccccccccc} & H & & H & & H & & H & \\ & | & & | & & | & & | & \\ H- & C & - & C & - & C & - & C & -H \\ & | & & | & & | & & | & \\ & H & & H & & H & & H & \end{array}$, often shortened as we have seen to $CH_3[CH_2]_2CH_3$. Quite right. But what about the formula  $\begin{array}{ccccccc} & & & \alpha & & & \\ & H & & H & & H & \\ & | & & | & & | & \\ H- & C & - & C & - & C & -H \\ & | & & | & & | & \\ & H & H- & C & -H & H & \\ & & & | & & & \\ & & & H & & & \end{array}$ or $CH(CH_3)_3$? (Never mind the 'α' for the present.) Careful inspection shows that we have certainly kept to the rules. It seems then that 4 carbon atoms and 10 hydrogen atoms can be arranged to give two different kinds of molecule, though both are 'C_4H_{10}.' But different molecules should correspond to different substances. Are there then *two* butanes? The answer is 'Yes.' Both are gases, one ('butane,' 'normal butane' or '*n*-butane') boiling at – 1° C., the other, *iso*butane at – 11° C. As their boiling points are not much below 'ordinary' temperatures they readily liquefy under slight pressure, becoming gaseous when the pressure is released. This property is utilised in the well-known 'Calor gas,' which consists largely of the substances just mentioned, mixed with certain other hydrocarbons. When two or more substances exist having the same molecular formula, they are known as *isomers* or *isomeric forms.* Thus we say there are two isomers having the same molecular formula C_4H_{10}.

We pass on to the next member of the series, pentane, C_5H_{12}. We get the straight-chain formula easily enough—'normal' pentane—which we will shorten to $CH_3[CH_2]_3CH_3$. Call this 'formula I.' To explore the other possibilities, unless we want to land in hopeless muddle, we must go to work systematically.

Turn back to the last structural formula, that for *iso*butane. The unmarked hydrogen atoms are really all similar—each of them is attached to a carbon atom which is itself attached to one other carbon atom. The 'α' hydrogen atom is different, for it is attached to a carbon atom which is itself attached to *three* other carbon atoms. Now to get from C_4H_{10} to C_5H_{12}, replace any one of the unmarked atoms by CH_3. The results will be really the same, whichever atom you replace, because these atoms are similarly placed. As a result we get formula II below.

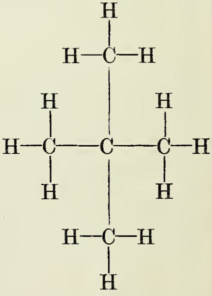
Now go back to the C_4H_{10} structure, this time replacing the 'α' atom. The result is formula III.

II



or $CH(CH_3)_2\cdot CH_2(CH_3)$

III



or $C(CH_3)_4$

Thus according to theory, three isomers of molecular formula C_5H_{12} should exist—*and three are actually known.*

You may like to amuse yourself by working out the formulæ for all the possible hexanes, C_6H_{14}. You should find that there are five, and here again five are actually known. This correspondence between the number of isomers theoretically possible and the number actually known is, of course, a tremendous support to the theory that the carbon atom is really tetravalent.

You will not be surprised to learn that a point is soon reached at which the number of known isomers is always less—and soon very much less—than the number theoretically possible.[1] It does not mean, of course, that the theory has broken down, but only that no scientist is going to spend a lifetime in preparing or isolating them. For the hydrocarbon $C_{13}H_{28}$ it seems that no less than 802 isomers are theoretically possible, but only the normal one, $CH_3[CH_2]_{11}\cdot CH_3$, is actually known.

We can easily see that though the number of carbon compounds would have been very great simply because of the chain-forming tendency of the atom, this great number is vastly increased by the existence of isomers.

Where the chain is long enough, inorganic compounds can, of course, exist in isomeric forms, but because such chains are seldom very long, the number of isomers is seldom large.

You will have noticed that the hydrocarbons we have been discussing form a regular series, each member of which has one carbon atom and two hydrogen atoms more than the preceding one. The series can in fact be expressed by the general formula C_nH_{2n+2}, where n has all values from 1 to about 60. It is known as the *paraffin* series (paraffin = small affinity), because its members are not on the whole very reactive chemically. Crude oil is a mixture of very many of them, and on p. 205 we have already said something of the way in which it is separated into its constituents, among which 'petrol' is very prominent. The demand for 'petrol' is, of course, very great, and large additional supplies are obtained by the

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[1] According to *Encyc. Brit.*, the limit of correspondence seems to have been reached with nonane C_9H_{20} (35 theoretical structures, and 35 compounds identified).

'cracking' of the higher hydrocarbons. We shall say something about this presently.

It is one characteristic of a pure solid substance that it has a sharp melting-point. Naphthalene for instance (m.p. 79°), would be solid at 78½° and liquid at 79½°. When ordinary paraffin wax is heated it passes through a soft stage when it is impossible to say whether it is solid or liquid—its melting-point is not 'sharp.' The reason is, of course, that it is a mixture, not a single substance.

Alcohols. From methane, CH_4, we can by indirect means obtain *methyl alcohol*, CH_3OH, and from ethane, C_2H_6, *ethyl alcohol*, C_2H_5OH, the univalent —OH group replacing —H in each case. Methyl alcohol is often known as wood spirit, because it was formerly extracted from the liquid obtained by the destructive distillation of wood. It is much used as a solvent, and for adding to ethyl alcohol with a view to making the latter undrinkable (i.e. it turns it into *methyl*ated spirit).

When the word alcohol is used without qualification, ethyl alcohol is understood. It is easily prepared in the laboratory by dissolving 50 gm. of glucose in 10 times its weight of water in a large flask, adding yeast ('brewer's' for preference), and leaving the mixture in a warm place to ferment. There is much frothing, and if the gas evolved is passed into lime-water the latter turns milky. The reaction is expressed by the equation

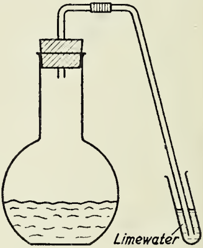

FIG. 19/1

$$C_6H_{12}O_6=2C_2H_5OH+2CO_2$$

After 24 hours or so the flask is attached to a Liebig's condenser and the first 20 c.c. distilled off (fig. 8/7, p. 87). The distillate contains alcohol mixed with much water. Most of the latter may be removed by adding a very strong solution of calcium chloride, shaking well and allowing to settle. The heavy, aqueous solution is run off by means of a separating funnel (fig. 19/2), the alcohol being left behind. At this stage it is well for several workers to pool their supplies. The collection is redistilled, but the flask is first fitted with a thermometer, the bulb of which comes opposite to the outlet tube. When the temperature rises to 85° the process is stopped.

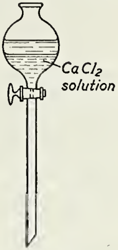

FIG. 19/2

The product still contains a small proportion of water, nearly all of which may be removed by leaving overnight in contact with small pieces of quicklime, filtering and redistilling. The thermometer should now record 78° C., the boiling point of alcohol.

Alcohol is a colourless, pleasant-smelling liquid. It burns with a nearly colourless flame, forming water and carbon dioxide, and (as methylated spirit) is often used as a fuel. On p. 197 we saw that with sulphuric acid it may give the gas ethylene, C_2H_4.

We cannot here go into the question of how alcoholic drinks are made, except to say that the preparation includes a fermentation process similar to the one already described. During fermentation the percentage of alcohol never rises above 18, because at higher concentrations the yeast cells cease to act. The product may, however, be distilled, producing *spirits* (brandy,[1] whisky, rum, etc.), in which the percentage of alcohol may, of course, be much higher.

Most governments put a very heavy tax on alcohol, thus raising money and at the same time discouraging excessive drinking. It happens, however, that alcohol is needed for many industrial operations—the extraction of oils and the preparation of ether and chloroform to mention only one or two—and the government does not wish to discourage these. The difficulty is fairly well overcome by allowing alcohol to be sold free of duty provided it has been 'denatured' or 'methylated' by the addition of wood spirit, as already mentioned, together with paraffin, bone oil, etc., and, usually, a violet dye. These additions make it extremely unpalatable, without interfering with its legitimate use.

In a moment we shall be considering *acetic acid*, so we may mention here that this substance is formed when a mixture of air and alcohol vapour is passed over platinised asbestos, the alcohol undergoing oxidation at the surface of the platinum:—

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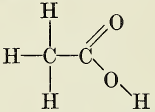
[1] Brandy was formerly *brandwine*—wine that has been 'burnt' or distilled.

$$C_2H_5OH + O_2 = C_2H_4O_2 + H_2O$$

Acetic Acid. The chemical change just mentioned indicates that acetic acid may be regarded as an oxidation product of alcohol. The same point is illustrated by the fact that beer and wine residues, if left exposed to the air for some time, become sour. This principle is applied in the manufacture of vinegar, which contains about 5 per cent. of acetic acid (vinegar = *vin aigre*, sour wine).

Pure acetic acid consists of colourless crystals melting at 16·7° C., so in cold weather it is solid, in warm weather liquid. Its structural formula is  , usually shortened to $CH_3{\cdot}COOH$. It is only the hydrogen in the 'carboxyl' group, $-COOH$, that is replaceable by metals in the formation of salts, the *acetates*. Thus sodium acetate would be $CH_3{\cdot}COONa$ (p. 196), and lead acetate $(CH_3{\cdot}COO)_2Pb$, lead being divalent.

The formula of alcohol, C_2H_5OH, reminds us of that of the base sodium hydroxide, NaOH, and indeed alcohol does in some ways resemble a base, though it has no effect on litmus. With acetic acid under certain conditions we have the reaction

$$\underset{\textit{Acetic acid}}{CH_3{\cdot}COOH} + \underset{\textit{Alcohol}}{C_2H_5OH} = \underset{\textit{Ethyl acetate}}{CH_3{\cdot}COOC_2H_5} + \underset{\textit{Water}}{H_2O}$$

(Notice the name *ethyl* given to the radical C_2H_5.[1] *Ethyl* alcohol, C_2H_5OH; *ethyl* acetate, $CH_3{\cdot}COOC_2H_5$, etc.)

The equation last given reminds us very much of that for the formation of a salt from an acid and an alkali (cf. $HCl + NaOH = NaCl + H_2O$). Actually, ethyl acetate is a colourless liquid with a smell that suggests 'pear drops'—not at all like a salt. It is known as an *ester*.

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[1] A *radical* is a group of atoms occurring in a number of different compounds, and forming a unit which behaves like a single atom. Thus it has a definite valency. Well known inorganic examples are ammonium, NH_4, and nitrate, NO_3 (valency 1); sulphate, SO_4 (valency 2).

Other Alcohols and Acids. You will already have guessed that if from methane, CH_4, and ethane, C_2H_6, we can derive methyl alcohol, CH_3OH, and ethyl alcohol, C_2H_5OH, there should be other alcohols derivable from propane, butane, etc. (and those isomers!) That is quite correct—there is a tremendous range of 'monohydric' alcohols as they are called, i.e. alcohols formed by substituting one hydroxyl group, OH, for one atom of hydrogen in the hydrocarbon.

Sometimes more than one such group is substituted, and because of their practical importance we must just notice the dihydric alcohol *ethylene glycol*, $C_2H_4(OH)_2$, and especially the trihydric alcohol *glycerol*, or *glycerine*, $C_3H_5(OH)_3$. The former gets the first part of its name because it can be regarded as an addition compound of ethylene, C_2H_4. You will see motorists, when cold weather is threatened, assiduously pouring a quantity of it into the radiators of their cars; it is an *antifreeze*. You have, of course, met with glycerine—a thick very sweet liquid with certain medicinal uses. With its formula of $C_3H_5(OH)_3$ we may regard it as glyceryl hydroxide, the 'radical' C_3H_5 being known as *glyceryl*, just as the radical C_2H_5 is known as *ethyl*. Notice, however, that while ethyl is univalent (combining with only one OH group), glyceryl is trivalent (combining with three). This point will crop up again, almost at once.

Acetic acid, $CH_3{\cdot}COOH$, is just the second[1] of a series which continues as $C_2H_5{\cdot}COOH$, $C_3H_7{\cdot}COOH$ and so on. The general formula is $C_nH_{2n+1}COOH$, each member being formed in the usual way by adding CH_2 to the preceding one. We might notice one or two of the higher members. There is stearic acid (pr. stee-ar′-ic), $C_{17}H_{35}COOH$, whose glyceryl derivative or *glyceride*, $(C_{17}H_{35}COO)_3C_3H_5$, is an important constituent of mutton fat, while the glyceride of palmitic acid, $(C_{15}H_{31}COO)_3C_3H_5$, occurs largely in palm oil, palmitic acid having the formula $C_{15}H_{31}COOH$. Because the higher members give rise to fats, the name *fatty acids* has been applied to the whole series.

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[1] The first is formic acid, $H{\cdot}COOH$ (cf. p. 188).

The formulæ just given look alarming at first, but as the groups $C_{15}H_{31}COO$— and $C_{17}H_{35}COO$— are univalent, while as we saw a moment ago $C_3H_5\equiv$ is trivalent, we can account for them easily enough.

If in stearic acid, $C_{17}H_{35}COOH$, the hydrogen of the COOH group is replaced by sodium, we get sodium stearate, $C_{17}H_{35}COONa$, which is a good *soap*. It is formed when mutton fat is boiled for some time with caustic soda solution.

$$\underset{\textit{Glyceryl stearate}}{(C_{17}H_{35}COO)_3C_3H_5} + \underset{\substack{\textit{Sodium}\\ \textit{hydroxide}}}{3NaOH} = \underset{\substack{\textit{Glyceryl}\\ \textit{hydroxide}\\ \text{(glycerine)}}}{C_3H_5(OH)_3} + \underset{\substack{\textit{Sodium}\\ \textit{stearate}}}{3C_{17}H_{35}COONa}$$

After the boiling has continued for a while, a strong solution of common salt is added, and this causes the soap to separate out. If palm oil is used, the soap obtained is sodium palmitate, $C_{15}H_{31}COONa$. Try the equation for yourself. In spite of the big numbers, you will not find it too difficult if you keep clearly in mind that 'glyceryl' is trivalent, while the other reacting atoms or groups, $C_{15}H_{31}COO$—, Na— and —OH, are all univalent.

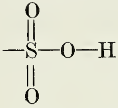
As we saw on p. 180, troubles arise when soap is used with hard water (water containing a calcium compound such as the sulphate, $CaSO_4$). The soap reacts with the calcium compound, forming calcium stearate:—

$$\underset{\textit{Sodium stearate}}{2C_{17}H_{35}COONa} + \underset{\substack{\textit{Calcium}\\ \textit{sulphate}}}{CaSO_4} = \underset{\textit{Calcium stearate}}{(C_{17}H_{35}COO)_2Ca} + \underset{\substack{\textit{Sodium}\\ \textit{sulphate}}}{Na_2SO_4}$$

Because it is insoluble, the calcium stearate forms a white precipitate, which you can see floating about after you have been washing your hands in hard water. Not until all the calcium present has been turned into calcium stearate (at the expense of the soap) can the soap begin to act as a cleansing agent.

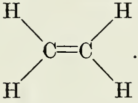
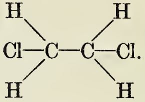
If only there were some kind of soap which formed a *soluble* calcium compound instead of an insoluble one! It could then do its work, even in hard water.

There are such soaps, usually known as *detergents*. You can see them advertised everywhere, each one apparently washing whiter than its rivals. Let us look into the question.

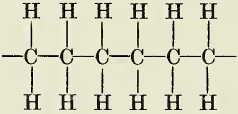
The organic 'acid' radical we have so far considered is —COOH. This 'carboxyl' radical is much the commonest, but is not the only one. For our present purpose we are concerned with the 'sulphonate' radical  $-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O-H$ or $-SO_2OH$ (sulphur here has a valency of six). As in the case of the COOH radical, the 'H' is replaceable by 'Na,' forming sodium salts. Now these sodium salts may be prepared from the long-chain hydrocarbons present in crude oil, and their formulæ may be written $CH_3[CH_2]_nSO_2{\cdot}ONa$, where n has values from 11 to 17. It will be a useful little exercise for you to write the formula in full for the case in which, say, $n=14$.

Most detergents may be said to follow this general pattern, but, usually, they also contain more ordinary salts, such as sodium carbonate and sodium phosphate (p. 364).

As compared with soap, they possess two very solid advantages. First, the raw material for their manufacture is crude oil, while soap is made chiefly from fats or oils which are easily turned into foods, such as margarine. In short, the making of soap makes inroads on the world's food supplies, while that of detergents does not. The other advantage has already been mentioned—the detergents can be used with hard water.

Unsaturated Hydrocarbons. On p. 198 it was explained that ethylene, C_2H_4, is an *unsaturated* hydrocarbon, with the structural formula  . The double bond between the carbon atoms does not mean that the latter are united with special firmness. It *does* mean, however, that there is a valency bond in reserve, so to speak, and so ethylene readily forms *addition* compounds, such as $C_2H_4Cl_2$, $C_2H_4(H)(HSO_4)$, etc. (it is readily absorbed by sulphuric acid). The structural formula for the dichloride would be . The double bond has disappeared, and we have a *saturated* compound. Notice that these extra atoms or groups can be taken on only in *pairs*. When the reserve valency comes into play from the one carbon atom, of necessity it comes into play from the other. Ethylene is the first member of what is known as the *olefine* series, C_2H_4, C_3H_6, C_4H_8 . . . and generally C_nH_{2n}.

Now the ethylene molecule can combine not only with two atoms of chlorine, hydrogen, etc., it can combine with other ethylene molecules. In this way compounds are formed containing carbon chains of varying length such as



$$\begin{array}{cccccccccccccc} & H & & H & & H & & H & & H & & H & \\ & | & & | & & | & & | & & | & & | & \\ - & C & - & C & - & C & - & C & - & C & - & C & - \\ & | & & | & & | & & | & & | & & | & \\ & H & & H & & H & & H & & H & & H & \end{array}$$

Such a process (similar molecules combining with one another to form larger ones) is known as *polymerisation*. Under great pressure, ethylene can be made to form polymers in which the carbon chain is more than 1000 atoms long! The product is known as polythene, a 'plastic.'

There are other products too for which ethylene is the basic raw material. But where is any large supply of this raw material to be obtained? There is plenty of *methane* in coal-gas and the 'natural gas' from oil-wells, but not much ethylene.

We saw (p. 204) that crude oil contains many hydrocarbons of the paraffin series—C_5H_{12}, C_6H_{14}, C_7H_{16}, etc. When such oil is vaporised and strongly heated in the presence of a catalyst a process known as 'cracking' takes place, the 'long chain' hydrocarbons being broken down into simpler ones. We might have, for instance, $C_{11}H_{24} = C_7H_{16} + C_4H_8$, followed by $C_7H_{16} = 3C_2H_4 + CH_4$ and $C_4H_8 = 2C_2H_4$.

By careful control of the working conditions, a good deal of ethylene is produced and can be extracted. Still, the reactions are much more complicated than is suggested by the equations just given, and many other substances are produced. Among them are materials from which the fabric *terylene* is made.

The essential result of the cracking process is the formation of molecules with a smaller number of carbon atoms. Now, as we have seen, petrol is chiefly a mixture of paraffins having the formulæ C_6H_{14}, C_7H_{16} and C_8H_{18}. Crude oil contains many 'higher' paraffins, but by carefully controlled cracking these can be broken down, giving products which come, for the most part, within the ranges just mentioned. Thus petrol is obtained not only from the hexane, heptane, etc., originally present in the crude oil, but also from further supplies of these substances produced by cracking.

Unsaturated Acids. On p. 215 we saw that, connected with the saturated hydrocarbons, the paraffins (CH_4, C_2H_6, C_3H_8 . . . or, generally, C_nH_{2n+2}), there was a whole series of acids of the general formula $C_nH_{2n+1}\cdot COOH$, an example being stearic acid, $C_{17}H_{35}\cdot COOH$. Similarly, connected with the unsaturated hydrocarbons of which we have been speaking, the olefines of general formula C_nH_{2n}, there is a whole series of acids of the general formula $C_nH_{2n-1}\cdot COOH$. In Nature these are found as *glycerides*, i.e. combined with the glyceryl radical C_3H_5. Glyceryl oleate, for instance, would be $(C_{17}H_{33}COO)_3C_3H_5$, just as glyceryl stearate is

$$(C_{17}H_{35}COO)_3C_3H_5$$

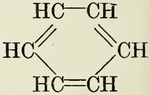
Glyceryl oleate is the chief constituent of olive oil and lard. Many of these oils are found as fish oils and whale oil. Until the beginning of the century they had very little value. They were too 'soft.' If they had been 'harder'—fats rather than oils—they could have been used in the manufacture of soap and margarine. Their fishy smell also made them very objectionable.

Now the corresponding saturated acids—acids with two extra hydrogen atoms—are usually solid fats. Could the unsaturated acids be made to combine with these two extra atoms? After many experiments the French chemist Sabatier of Toulouse found that they could. He used finely divided nickel as a catalyst, and the formerly despised fish oils now play an important part in the soap and margarine industries. It seems very unfair that although shareholders in industries connected with fats and oils have made fortunes out of Sabatier's discovery, the chemist himself received none of the proceeds. To quote from a lecture by Dr. E. F. Armstrong, 'Solid fats from liquid oils, edible fats from whale and fish oils, a fortune for the whaling industry made literally overnight, and yet I vouch that no captain of a whaler or shareholder in a whaling company has ever heard of the name of Sabatier.'

One is glad to learn, however, that he was awarded one of the famous Nobel prizes.

In passing we might just notice linseed oil, which consists chiefly of the glyceride of an unsaturated acid, linolenic acid, belonging to still another series. In this case the molecule actually contains a triple bond, so it is unsaturated to a specially high degree. It combines with oxygen at ordinary temperatures, forming a solid compound known as linoxyn. Hence the 'drying' of paints. The same chemical change is involved in the hardening of putty (linseed oil *plus* finely divided calcium carbonate) and in the making of linoleum (essentially linseed oil *plus* cork-dust).

Closed-chain Compounds. So far we have spoken only of 'open-chain' compounds, i.e. compounds in which the atoms are strung out in a line so to speak. But sometimes the chain is 'closed,' forming some sort of polygon. In the commonest case this is a hexagon. Thus benzene is represented by the formula with double bonds as shown. The formula has been the subject of a great deal of discussion into which we need not enter. We have mentioned the subject of closed-chain compounds, however, to show that here we have still another arrangement which adds to the already vast number of possible arrangements of atoms in organic compounds.



The Story of Vitamin B_1. In very brief outline we will here give the story of vitamin B_1, because it affords an excellent illustration of the kind of problem, or rather series of problems, with which the organic chemist often has to deal.

It begins in a prison in Java, where the medical officer, a man named Eijkman, was much worried by the prevalence of a serious disease called beri-beri among the men under his care. At the same time, curiously enough, many of the poultry in the prison grounds were dying from a complaint known as polyneuritis, characterised by paralysis and certain convulsive movements. After much careful observation and experiment, Eijkman showed that the beri-beri and the polyneuritis were due to the fact that both men and birds were being fed on polished rice—rice from which the husk and germ had been removed. When 'whole rice' was used instead, these diseases did not appear. This important discovery was made in 1897.

A few years later, in 1912, very similar discoveries began to be made in connection with scurvy and other diseases. It was concluded that a full supply of fats, proteins and carbohydrates—long recognised as the important constituents of a healthy diet—was not enough. Certain other substances, now known as *vitamins*, must be present in the diet. Usually the amount required is small in the extreme, but if they are completely absent something goes wrong—often seriously wrong—with the health of the person or animal concerned.

No doubt one of these vitamins was present in the husk of the rice grain. Now this husk would most likely contain a number of different substances, of which probably only one was concerned in the prevention of beri-beri, etc. So in 1912 chemists set to work to obtain this substance, the vitamin, in pure condition.

The general plan is easy enough to understand. By what we will call process No. 1 (actually this involved the use of china clay, but we are not concerned with the details), they divided the husk into two portions X_1 and X_2, just as we might by a much simpler process separate a mixture of sand and salt into two portions. Does X_1 contain the substance they are seeking, or does X_2? They dose polyneuritic hens, some with X_1, some with X_2. The first lot continue to be ill, the second lot recover. Clearly, the substance they want is present in X_2, which will contain it in greater concentration than did the original rice husks.

They now apply what we will call process No. 2 to X_2, dividing it into Y_1 and Y_2, and once more, by dosing the hens, find out which contains the vitamin—and so on. The principle seems simple enough, but in practice there were many difficulties and setbacks, and it was not until 1926, after fourteen years' patient work, that the mysterious substance was isolated. The men concerned were two Dutch chemists, Jansen and Donath, working in the same laboratory in which Eijkman had made his first observations. Vitamin B_1, as it is now called, was found to be a white crystalline substance, with a bitter taste, soluble in water.

The next step—to find the elements present in it—is a very simple one. It turned out that besides carbon there were present hydrogen, oxygen, nitrogen, chlorine and sulphur. To find the percentage of each is no very formidable task. The results obtained were carbon 42·7, hydrogen 5·3, oxygen 4·8, nitrogen 16·6, chlorine 21·1, sulphur 9·5. If you have remembered what you learnt in Chapter 5, you can work out the 'simplest formula' for yourself. You should get $C_{12}H_{18}ON_4SCl_2$.

As you know, the simplest formula is not necessarily the molecular formula. If, for instance, we were asked to find the simplest formula of a hydrocarbon containing 80·0 per cent. of carbon and 20·0 per cent. of hydrogen, we should arrive at the answer CH_3. If we were told further that its vapour density was 15, we should conclude that its molecular weight must be 30 ($m=2d$, p. 126). But 'CH_3' would have a molecular weight of only $12+3=15$, so the formula must be C_2H_6.

Vitamin B_1 is a solid, not a gas, so we cannot find the molecular weight in the way just mentioned. There *are* methods, however, by which the molecular weight of a solid can be determined with fair accuracy, and for vitamin B_1 the number obtained was close to 337. Now this corresponds to the molecular weight for $C_{12}H_{18}ON_4SCl_2$, so the formula just given is the molecular formula as well as the simplest one.

Up to this point we have been able to follow fairly clearly the method of the research chemists. Now comes a problem which we can appreciate, though the method of solving it is much beyond the scope of this book. The problem is, 'How are the atoms *arranged* in this substance whose molecular formula has been found to be $C_{12}H_{18}ON_4SCl_2$?' In other words, 'What is the structural formula?'

Even for first-class chemists, the problem is not an easy one, and another nine years elapsed before it was solved. They arrived at the structural formula shown overleaf.

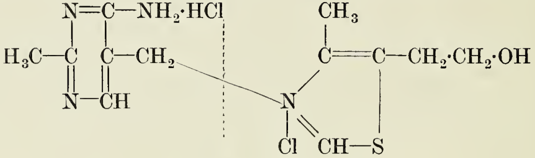
The pure vitamin is, of course, far more potent than the rice husks with which we started. Thus while a hen could be kept free from polyneuritis by a daily dose of 5 mgm. of the husks—the weight of a *very* tiny crumb—about $\frac{1}{400}$th of that quantity of pure vitamin B_1 was sufficient. For a man, about 1 mgm. per day would keep him free from beri-beri.

After twenty-three years of research—fourteen to isolate the substance and nine more to establish its structural formula —has the chemist finished his job? Not yet. Here is a substance which, with all its complications, after all contains only six very common elements. The chemist feels that he ought to be able to *make* vitamin B_1 from carbon, hydrogen, oxygen, etc., or at least, from simple compounds which he could if required make from these elements. In short, he feels that he should be able to *synthesise* the compound.

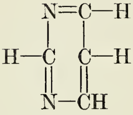
Suppose a clever mechanic were given a clear drawing of a bicycle and were asked to construct one—the construction corresponding to synthesis, and the drawing to the known structural formula. 'What can you provide me with?' he asks. Now if he is told that he can have only an ingot of steel, sheets of rubber and some leather (for the saddle), etc., with no prepared parts whatever, his task would be formidable indeed, though not utterly impossible. This corresponds to what the chemist's task would be if he had to start from the elements carbon, hydrogen, etc.

But suppose we say to our mechanic, 'In the yard here you will find all sorts of odds and ends. Bicycle wheels with tyres on them, old saddles, handlebars, mudguards . . .' He brightens up at once and can set to work hopefully.

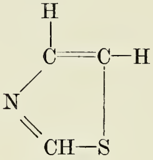
Now that is very much the position of the chemist who knows the structural formula of the compound he wishes to synthesise. The mechanic hopes to find this or that part—a wheel, a saddle, a handlebar—already made. So does the chemist. Looking carefully at the structural formula, he says, 'I think that part to the left of the dotted line might be prepared from pyrimidine, and that on the right from thiazole,' pyrimidine and thiazole being substances already familiar.



Vitamin B_1 (thiamine)



Pyrimidine



Thiazole

It may take him a very long time to change pyrimidine and thiazole into what he wants, and even when he has done so, his 'left' and 'right' compounds may decline to link up to form the complete structure. Actually, complete success was attained after about two years work. At the present time, though some vitamin B_1 is still prepared by extraction processes from rice husks, yeast, etc., the greater part is made synthetically. There is no difference whatever between the products, whether obtained by extraction or by synthesis.

Sometimes the discovery of a synthetic method has had most astonishing results. Thus after fifteen years' work, Baeyer and others discovered how to synthesise indigo, using naphthalene ('moth-balls') as the substance to start from. Until 1897 indigo was prepared exclusively from the indigo plant, which grows in India. But in spite of the very low cost of labour in that country, synthetic indigo could be manufactured at less than half the price. Thus a million acres of land formerly required for the cultivation of indigo can now be used for the production of other crops.

On the other hand, a synthetic process is sometimes more costly than the 'natural' one. The production of penicillin is a case in point.

We must now conclude our very brief survey of Organic Chemistry. At least, we now have a clear idea of the meaning of the term, and of that chain-forming property of the carbon atom which leads to such astonishing results. Also perhaps, we have acquired a deepened admiration for the patience and skill of men who devote years of their lives to clearing up first one and then another of the mysteries of nature, and in so doing add in many cases to the health and comfort of their fellows.

Questions

1. What do you understand by the terms *simplest formula, molecular formula, structural formula*? Illustrate your answer by reference to the formula of acetylene.

2. Give *two* reasons why compounds containing carbon are far more numerous than compounds not containing it.

3. How could a small specimen of ordinary alcohol be prepared in the laboratory? Mention one point of resemblance and one point of difference in chemical behaviour between this substance and sodium hydroxide.

4. How could soap be made from mutton fat? Give the chemical names of the reacting substances and of the products.

5. Give some account of the chemical nature of a modern detergent. What advantages does it possess over ordinary soap?

6. Explain briefly what is meant by (*a*) isomerism; (*b*) the paraffin series; (*c*) an unsaturated hydrocarbon; (*d*) the cracking of crude oil.

7. At the top of p. 218 there is given the structural formula of 'ethylene chloride,' $C_2H_4Cl_2$. It is a colourless liquid with a sp. gr. of 1·265, boiling at 84° C.

Another compound is known, however, with the same molecular formula $C_2H_4Cl_2$, but with a sp. gr. of 1·178 and b. p. 59° C.

Account for the existence of this second compound. Give reasons for believing (or not believing) that there may be still other compounds having this same structural formula.

CHAPTER 20

COMBUSTION, FLAME AND INCANDESCENCE

Combustion. All chemical changes are accompanied by the giving out, or the taking in, of heat. Sometimes the heat produced is so great that light is given out as well. For instance, you will remember the red glow produced when iron and sulphur are heated together, and of course light is produced during the burning of an ordinary fire, or when magnesium, sulphur, etc., burn in oxygen. Such chemical changes are examples of ***combustion,*** which is usually defined as *chemical action accompanied by light and heat.* Sometimes, as in the case of the steam-engine or motor-car, the object is to convert as much as possible of the heat of combustion into mechanical energy.

As we think of the common fuels—coal and coke, paraffin, producer-gas, water-gas and so on—we notice that carbon is always present, and usually hydrogen. When combustion is complete, these become carbon dioxide and water respectively. Unfortunately combustion seldom *is* complete. In particular, some part of the carbon escapes oxidation, with the disastrous results of a smoke-laden atmosphere and the blackening of buildings, besides the constant necessity for sweeping chimneys and (in the case of the motor-car) decarbonising.

In some cases, substances such as tar, oil, resin, etc., are burnt in a supply of air which is purposely limited, in order that lampblack (a variety of 'amorphous carbon') may be obtained.

Incomplete combustion may result in the production of the very poisonous gas carbon monoxide. This is very marked in the case of the motor-car, where the exhaust gases often contain some 10 per cent. of carbon monoxide. We have seen (p. 185) that in the burning of a good fire this gas is produced only at an intermediate stage, and is oxidised later to carbon dioxide. In certain cases, however (besides that of the motor-car just mentioned), carbon monoxide certainly does escape into the air. This happens, for instance, when the air-inlet of a stove had been nearly closed for some time. On opening the top, to add fuel, one often notices a sudden 'pop,' with the formation of a blue flame as the carbon monoxide ignites. When the top was closed this carbon monoxide must have been passing unburnt into the flue.

Incomplete combustion is undesirable not only because of the production of much dirt (carbon) and some poison (carbon monoxide), but also because it represents a waste of the heat we should have obtained if this carbon or carbon monoxide had been completely burnt to carbon dioxide. Thus we see the great importance of arranging that combustion shall be as complete as possible, and when we can, of using fuels such as coke which burn with the production of little or no soot.

The remainder of this chapter will be concerned mainly with the combustion of gases. The burning of coal-gas in air is a very familiar example. Where, as in this case, one gas (air) entirely surrounds the other (coal-gas) the surrounding gas is known as the ***supporter of combustion.*** It is quite easy to turn the arrangement inside out, so that air becomes the burning substance while coal-gas is the supporter of combustion. To do this, a wide lamp-chimney is fitted with a cork bored with two holes, through which pass two tubes, a narrow one A bent at right angles, and a straight one B. The top is closed by a cork through which passes another glass tube C. C is closed with the finger while the chimney is filled with gas (air and surplus gas escaping through B). When the air has been expelled, a light is placed at the lower end of B, and of course the escaping gas burns. On opening C, air is drawn in through B and the flame travels to the other end of the tube. It now continues to burn as a non-luminous flame of air surrounded by coal-gas. The surplus gas may be lit at C, when we have the usual flame of coal-gas surrounded by air.

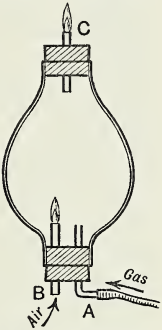


FIG. 20/1. Air burning in coal-gas

Flame. Everybody knows what is meant by a flame, though most people would be rather puzzled if they were asked to give an exact definition. We will consider this point a little later in the chapter.

One of the simplest flames to study is that of hydrogen. In broad daylight this is nearly invisible, but in semi-darkness it is fairly easy to examine it. It is then found to consist of two parts, A and B, as shown in fig. 20/2. Inside A it is comparatively cool, as we can easily show in several ways. We can put a piece of cardboard across the flame, in the position indicated by XY, and hold it there for a second or two. On withdrawing it, the cardboard is found to be charred only where it has been in contact with the *outer* portion. Or we can take a porcelain rod, such as is used for supporting an incandescent gas-mantle, and hold the tip of it in various parts of the flame. In some parts the tip glows very brightly, but inside A it does not glow at all. It is possible even to hold the head of a match inside A without its taking fire.

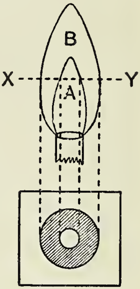


Fig. 20/2
Hydrogen flame

Of what does A consist? Using a short tube of hard glass, it is possible by placing it as shown in fig. 20/3 to light gas escaping at D. Clearly the part A consists of unburnt hydrogen.

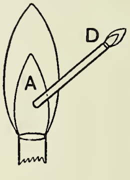


Fig. 20/3
A consists of unburnt hydrogen

We must now consider the part B. Exploring it with the porcelain rod, we soon find that it is very *hot*. It might seem nearly impossible to find out what is going on in the part B, and yet it is really very easy. The experiment illustrated by fig. 10/2 (p. 112) shows that just *outside* B water-vapour is present, while the experiment with the hard-glass tube, described a moment ago, shows that on the *inner* side of B hydrogen is present. It is very evident, then, that this outer portion of the flame must be the place where hydrogen is combining with oxygen, forming water.

The flame of carbon monoxide, with its intense blue colour, is much easier to see than the hydrogen flame. It is made up of two parts, however, in exactly the same way, and fig. 20/2 will serve to represent a flame of carbon monoxide just as well as one of hydrogen. It is not at all difficult to show that on the inner side of B there is unburnt carbon monoxide, and on the outer side there is carbon dioxide. In B, then, carbon monoxide must be combining with oxygen to form carbon dioxide.

We must now consider the candle flame. If you light a candle and ask a friend how many parts he can see, it is very likely that he will answer 'Three.' There is a dark part, A, round the upper portion of the wick and extending above it. Surrounding this, except at the bottom, there is a bright yellow part, B—the part that gives off the light. Round the base of the wick is a bright blue portion, C. This can be traced, as an outer edge to the flame, to about the level of the top of the wick.

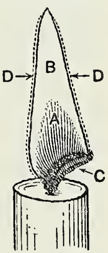


FIG. 20/4
Candle flame

There is, however, a fourth part, D, a narrow and almost invisible fringe indicated by the dotted line in fig. 20/4. If you look very intently you can just make it out, or if you sprinkle a little salt into the flame it turns yellow just for an instant, and so becomes visible.

Let us now try to understand what is happening in these various parts. We must begin with the fuel—the wax of which the candle is composed. This consists chiefly of a number of hydrocarbons, the substances we considered in the last chapter. Candle-wax contains scores of these compounds.

The wax is melted and drawn up by the wick by what is called 'capillary attraction.' This liquid then *vaporises*, just as water might be turned into steam, and the dark part, A, is filled with the vapour. A might be called the *zone of vaporisation.*

In B the hydrocarbons are *decomposed* into hydrogen and carbon. The free carbon in B plays a very important part, for each tiny speck, being very hot, is *incandescent*, i.e. it gives out light. The total light of the candle is made up of all the tiny portions of light given out by these countless specks of carbon.

The hydrogen and the carbon particles present in B are constantly drifting outwards, and at D they come into contact with the oxygen of the air. The result is that the hydrogen combining with the oxygen forms water, while the carbon is turned into carbon dioxide.

An examination with the tip of the porcelain rod shows that the lower blue part, C, is particularly hot. No doubt this is a part where oxidation is taking place with unusual vigour. A little thought suggests the probable reason. Everywhere in the close neighbourhood of the candle flame there must be air-currents ascending vertically as the result of convection. The lower part of the flame 'faces' these currents, and so receives a particularly good supply of air. Further, the air reaching the lower part still possesses its full proportion of oxygen. The upper part of the flame is fed with air which has lost some of its oxygen to the lower part.

We may sum up our results by saying that

A is the zone of *vaporisation.*
B ,, ,, *decomposition.*
C and D are zones of *oxidation.*

It is more correct, however, to call B the zone of *decomposition and partial oxidation*, because a little air drifts inwards to B. This oxidises a small portion of the hydrogen (to water) and a little of the carbon (to carbon monoxide).

Clearly there must be an increase in weight while a candle is burning, for during the process the elements present are combining with oxygen. This increase can be shown by the experiment illustrated in fig. 20/5. The upper part of a light lamp-chimney is loosely filled with large pieces of quicklime, topped with a layer of coarse soda-lime. A piece of wire-gauze is stuffed in at A to prevent the quicklime from falling out. The lower half of the chimney is closed with a cork carrying a short piece of candle, plenty of holes being bored in the cork to supply air for the burning of the candle. With the help of some wire, the chimney is suspended from the hook of a balance. The whole is counterpoised, after which the candle is lighted. The carbon dioxide and water produced are absorbed by the quicklime, and in the course of a few seconds an increase in weight begins to be indicated.

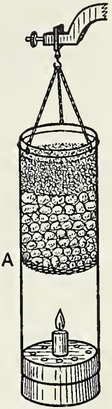


Fig. 20/5. Products of combustion weigh more than the candle

You are probably aware that until 1840 or so it was constantly necessary to 'snuff' a candle. The wick stood straight up and did not burn away. As the candle grew shorter the wick soon reached up to, and beyond, the top of the flame. It also grew thicker with the soot that gathered round it, and unless this long, thick wick was constantly nipped off, the flame soon became dim. Why do we never need to snuff a candle in these days?

We have seen that a candle flame is constantly giving off carbon dioxide and steam. The tip of a straight wick, sticking up through the middle of the flame, is surrounded by a stream of these gases and does not obtain the oxygen that would be necessary to burn it away. The difficulty was surmounted by *plaiting* the strands of the wick instead of merely twisting them together. The plaited wick is flat, and bends over so that its tip is always in a part of the flame which receives plenty of oxygen; hence it is constantly burnt off. It is rather surprising that our ancestors, who were far more dependent on candles than we are, never learnt to make a good one.

We now come to the old-fashioned 'fishtail' burner, still occasionally used in a scullery or bathroom. We can make out four parts very similar to those in the candle flame. A is the zone of unburnt gas corresponding to the zone of vaporisation. In B the hydrocarbons present in the gas are decomposed, and as before we have present free carbon particles which become incandescent. C and D are zones of oxidation.

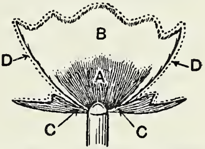


Fig. 20/6. Fishtail burner

By making the gas issue from a narrow slit the flame acquires a flat shape, and a larger surface is presented to the air. The result is that the whole series of chemical actions can go on at a greater rate, and so a better light is obtained.

The Bunsen Flame. The gas flame just described would not be very suitable for laboratory work. As we have seen, there is free carbon—soot—in the part B, and so any apparatus heated with such a flame would soon be blackened. In 1855 Robert Bunsen invented the improved burner which bears his name, and which you can easily examine for yourself. The gas is delivered through a fine orifice, O, and as it rushes out, air is sucked in through an inlet just opposite to it. By moving a metal collar the air-inlet can be opened to any desired extent, or can be closed altogether.

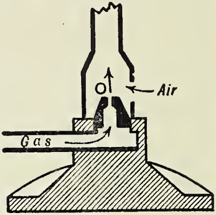


Fig. 20/7. Bunsen burner

In the bunsen flame we can distinguish three parts

A. A dark inner cone of unburnt gas. This is surmounted by

B. A greenish-blue sheath, where partial oxidation is taking place. Outside this is

C. A pale blue outer zone, where oxidation is completed.

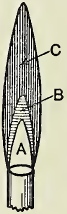


Fig. 20/8 Parts of bunsen flame

The fact that the bunsen flame gives practically no light was formerly explained in a very simple way. A flame gives light (as we have seen) because of the presence of free carbon particles. When air is mixed with the gas, the carbon particles (it was said) are instantly burnt away to carbon dioxide. The absence of carbon particles also causes the flame to be free from soot.

In 1892, however, a man named Lewes thought he would try the effect of so arranging a bunsen that other gases instead of air should be sucked in at the bottom—he tried nitrogen for instance. The luminosity was still destroyed! It is quite evident that here there is no question of the carbon particles being oxidised in the interior of the flame. It may be that

(1) When the bunsen is used in the ordinary way (air drawn in at base) the old explanation as just given is the correct one.

(2) When nitrogen or other inert gas is introduced, the cooling action is the chief factor, preventing the temperature (in the region where otherwise the hydrocarbons would have been decomposed) from rising high enough for decomposition. Thus there would be no inner zone containing free incandescent carbon particles, and no considerable chemical change until the mixed gases (hydrocarbons plus nitrogen, etc.) meet the outer air, where simultaneous decomposition and oxidation would take place.

This explanation receives some support from the fact that, when an inert gas is drawn in, the flame shows only *one* zone, apart from the zone of unburnt gas.

It is perhaps hardly necessary to say that when the air-inlet at the base of a bunsen burner is closed we have nearly the state of things already described in connection with the fishtail burner, the differences being that

(*a*) in the absence of the 'narrow-slit' arrangement the flame retains a roughly cylindrical shape instead of being flat, and

(*b*) there is no well-marked zone of specially complete combustion at the base (C in fig. 20/6).

Striking Back. If while keeping the air-holes open you turn a bunsen flame lower and lower, a point is reached at which it 'strikes back,' burning at O with an unpleasant smell. Why should this happen?

Remember that the barrel of the bunsen burner contains a mixture of gas and air, and flame always tends to pass through such a mixture. Thus there is always a *tendency* for the flame to travel down the tube, but in an ordinary way the gas is travelling up the tube as fast as the flame can travel down. Hence the flame can make no progress downwards—

it is like a swimmer unable to make headway against a strong current. When you reduce the speed of the upward stream of gas the flame can at length make headway, and you hear the familiar little 'pop.'

Definition of Flame. We are now in a position to give a very fair definition of the term 'flame.' Again and again we have noticed that in a flame chemical action is going on, in which gases are concerned; that heat is produced and usually some amount of light. We shall not be far wrong, then, if we say that ***flame** is a region in which chemical action is taking place between gases, with the production of light and heat.*

Applications of the Bunsen Flame. You have probably noticed for yourself that the bunsen flame is by no means confined to the laboratory. Every jet on the gas-oven at home consists of a little bunsen burner; so do the jets of a gas-fire; in fact, wherever gas is used as a source of heat, the bunsen principle is employed. We must now see how the bunsen flame is used as a source of *light*.

The Incandescent Mantle. It is a remarkable fact that the principle of the incandescent mantle was discovered (by Welsbach) in the very same laboratory at Heidelberg where Bunsen invented his famous burner. Welsbach was not trying to invent anything in particular. He was really observing the effects that could be obtained by heating certain salts in a bunsen flame, pretty much as you may have observed the yellow colour obtained by heating a sodium salt on a platinum wire. Welsbach, however, was obtaining his effects by dipping cotton threads in a *solution* of the salts he was using and introducing these into the flame. The cotton burnt away, leaving a kind of skeleton consisting of the dried salt (or rather of the oxide formed by the heating of the salt). This 'skeleton,' as we have called it, glowed with a very bright light, and this gave Welsbach the idea from which he was able to develop the incandescent mantle.

You can quite easily illustrate the principle for yourself. Add dilute nitric acid to powdered chalk—not quite enough to dissolve it. Soak in this a piece of rather open fabric—finger-bandaging does very well. Dry this gently, and afterwards hold the fabric in a bunsen flame. You will find you have got something which reminds you very much of a gas-mantle.

You will understand later that the nitric acid turned the chalk into calcium nitrate, and that the latter on heating became calcium oxide or quicklime. Thus, by indirect means, you have made a fabric of quicklime.

Gas-mantles, however, are not made of calcium oxide, but of a mixture consisting of 99 per cent. of thorium oxide and 1 per cent. of cerium oxide. As they would be much too frail for transport, they are dipped into a solution of collodion and then dried. The collodion stiffens them sufficiently for handling. It is this stiffening material which you have to burn off when you fix a new mantle in position.

For a given consumption of gas, the incandescent mantle gives something like six times the light obtained from the old fishtail burners. There is no doubt that as a lighting agent gas would long since have been superseded by electricity if it had not been for the discovery of the mantle, and this in turn was only made possible by Bunsen's invention thirty years earlier.

Questions

N.B. *See note in italics*, p. 132

1. Define *combustion*. How would you show that both carbon dioxide and water vapour are formed when a candle burns in air?

What volume of oxygen is required to burn completely, to carbon dioxide and steam, a mixture of 224 c.c. methane (CH_4) and 112 c.c. hydrogen? Assume that all volumes are measured at N.T.P. If the steam formed is condensed to water, what weight of this would be obtained? *Camb.*

2. Name the products of combustion of a candle in air.

Describe, with the aid of a diagram, an experiment which would demonstrate that the products of combustion of a candle weigh more than the candle itself.

Draw a candle flame and state briefly what is taking place in any *two* of the zones. *W.J.*

3. Explain why it is no longer necessary to snuff a candle.

4. How is a bunsen burner arranged to give its hottest flame? Draw a labelled diagram to show the regions that can be recognised in this flame. *Camb.*

5. Describe the flame produced by a bunsen burner when its air-hole is open. Account, as fully as you can, for what is observed when the air-hole is slowly closed. Under what conditions does a burner 'strike back'? Describe an experiment to show that it is possible to burn air in an atmosphere of coal-gas. *Lond.*

6. Who invented the incandescent mantle? Explain how he came to make the discovery. How could you illustrate for yourself the principle of the mantle?

7. Assuming that the gas-supply of a town consists of a mixture of hydrogen 60 per cent., methane 20 per cent. and carbon monoxide 20 per cent., and that air contains one-fifth its volume of oxygen, find the volume of air required for the complete combustion of 100 cu. ft. of the gas.

CHAPTER 21

COMMON SALT—HYDROCHLORIC ACID

Common salt is found in many parts of the world, and large quantities occur in our own country, notably in mid-Cheshire. It is present in thick beds, often two or three hundred feet below the surface. Holes are drilled into it and water is pumped in. After this has had time to become saturated with salt it is pumped out again and evaporated, the process being repeated again and again. Unfortunately this constant removal of salt leaves big holes inside the earth, and this causes the ground to subside, with disastrous results to the buildings. In Northwich (Cheshire) you will see chimneys ever so far out of the perpendicular, walls bulging forwards, window-sills level with the ground (or below it). In many cases houses have had to be abandoned altogether.

But not far from Northwich there are unsightly reservoirs ('lime beds') of waste material from the Solvay process (p. 418), and somebody had the bright idea of filling up the big holes by running in this waste mud. In the early 1950s a practicable scheme was worked out, so not only will the unsightly reservoirs disappear, but we may expect that in course of time the subsidences will cease.

Something should be said about the method of evaporation. This is usually carried out in 'vacuum pans,' in which advantage is taken of the fact that by reducing the pressure the boiling point of a liquid is lowered. In some of these pans the brine is actually boiling at a temperature of only 35° or so, which is barely the temperature of a hot bath. As compared with the old 'open pan' process, only about one-third of the amount of fuel is required. The old process is still used to some extent, however, because it yields large jagged crystals, which are preferred for some purposes, such as fish-curing.

'Rock salt' is obtained by mining, but there is now only one salt-mine worked in this country. It was started more than a hundred years ago. The workings cover more than 20 acres, and pillars of solid salt are left in position to support the roof. Rock salt is used as a fertilizer for certain crops (e.g. beetroot), for thawing snow and for various other purposes in which a high degree of purity is not necessary.

The salt industry is one of the most ancient in the country. Some of the lead pans have been found in which they used to boil a few gallons of brine over wood fires. The smaller one shown in the illustration is roughly 2 feet square, and probably dates from Saxon times, but the larger one may be as late as the seventeenth century. Output must have been on a very tiny scale. We now produce over 4½ million tons a year!

Properties. Salt crystallises in colourless cubes, without 'water of crystallisation.' It is only slightly more soluble in hot water than in cold. It has a rather high melting-point, 815° C., and is very *stable* (i.e. it can be raised to a high temperature without decomposition taking place). It is a necessary article of food. It is the starting-point in the manufacture of nearly all compounds of sodium, except sodium nitrate.

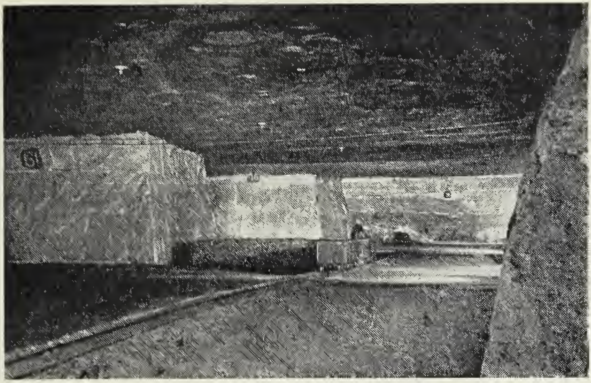
It is only very slightly soluble in hydrochloric acid, and advantage is taken of this fact when it is desired to produce a particularly pure specimen of the substance. A strong aqueous solution is made, and to this is added a quantity of concentrated hydrochloric acid. Pure salt at once crystallises out. This is filtered, washed with a little water and dried.

Hydrochloric Acid. When concentrated sulphuric acid is added to sodium chloride there is a rather violent effervescence, especially on warming, and a steamy-looking gas with a very pungent smell is evolved.

On passing the gas into water is readily dissolves, and the solution is strongly acid to litmus. When this solution is poured on zinc, hydrogen is evolved.

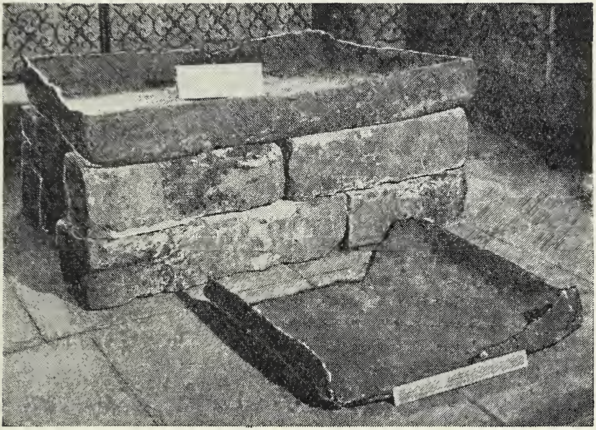
Assuming that zinc is an element, this gas must have come either from the gas or from the water in which the gas is dissolved. We can decide between these two possibilities by making the *dry* gas pass over heated zinc contained in a hard-glass combustion tube, and arranging to collect the emerging gas over water (which dissolves out excess hydrogen chloride). It proves to be hydrogen.

This experiment shows that the gas we are investigating contains *hydrogen*. Other experiments, to which we shall refer



By courtesy of Imperial Chemical Industries Ltd.

Britain's last salt-mine



By courtesy of Imperial Chemical Industries Ltd.

Lead pans formerly used for evaporating salt later (pp. 248, 393), show that when the hydrogen is removed, a greenish-coloured gas called *chlorine* is left. The latter gas proves to be an element. The gas which we are investigating, then, is a compound of hydrogen and chlorine. It is known as *hydrogen chloride*, its solution in water being called *hydrochloric acid.* It has been shown that its formula is HCl.

We now proceed to collect several jars of the gas, using the apparatus of fig. 21/1. The flask contains pieces of rock salt covered with concentrated sulphuric acid. If ordinary salt is used with undiluted acid the action is too vigorous, because the area exposed to the acid is much greater than when the salt is in the form of lumps; so with ordinary salt the acid should be *slightly* diluted (acid 2 volumes, water 1 volume—remembering to pour the acid into the water, and not vice versa.) If the gas is required *dry*, it is first passed through a U-tube containing calcium chloride, or pumice stone soaked in sulphuric acid, as shown in fig. 10/3 on p. 113; or it may be passed through sulphuric acid contained in a Woulff bottle, as shown in fig. 17/2 on p. 187.

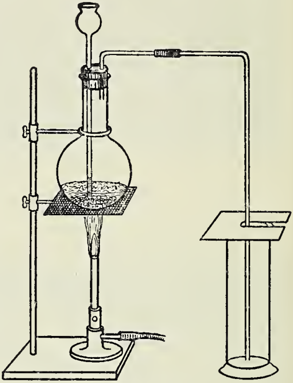


FIG. 21/1

At moderate temperatures the action is represented by the equation

$$NaCl + H_2SO_4 = \underset{\text{Sodium hydrogen sulphate}}{NaHSO_4} + \underset{\text{Hydrogen chloride}}{HCl}$$

Only one of the two hydrogen atoms is replaced, so that an *acid salt* is produced (p. 299). At higher temperatures than are usually employed in the laboratory both atoms are replaced, a *normal salt*, sodium sulphate (Na_2SO_4), being formed:—

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

If we wish to prepare hydrochloric acid (i.e. an aqueous solution of hydrogen chloride) the obvious course seems to be to pass the gas into water. It is so soluble, however, that there is considerable risk of 'sucking back.' To prevent this we adopt some such arrangement as that shown in fig. 21/2, or in fig. 23/3 on p. 266.

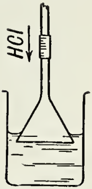


FIG. 21/2

Properties. The gas inside the flask is *colourless.* It is steamy, however, as it issues from the tube, owing to the presence of water vapour in the air. The gas dissolves in this water vapour, forming hydrochloric acid, minute drops of which give rise to the steamy appearance. It has a characteristic pungent smell and is heavier than air. Its great solubility in water is often shown by the 'fountain experiment.' A round-bottomed flask is fitted with a rubber stopper through which passes a glass tube. Inside the flask this tube is drawn out to a jet, while outside it is connected with a piece of rubber-tubing which can be controlled by a clip.

The flask is filled with the gas by downward displacement, and the stopper with its attachments inserted, the clip being closed. The flask is now placed with the mouth under water as shown in fig. 21/3, and the clip is removed. The water rises rather slowly at first, but when the water reaches the top of the jet the gas begins to dissolve in it very rapidly. This causes a great reduction of pressure inside the flask, and so the outside pressure drives the water with great force into the flask in the form of a fountain.

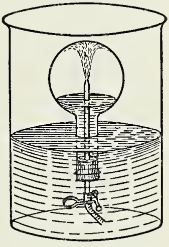


FIG. 21/3. The fountain experiment

The result is rather more striking if a quantity of blue litmus solution is first added to the water in the jar. On entering the flask the blue solution at once turns red.

Curiously enough, the *solution* of the gas was known long before the gas itself had been prepared. It was Priestley who first succeeded in really isolating the gas (1772). He heated hydrochloric acid in a flask, so arranging his apparatus that any gas given off should be collected over *mercury*. Earlier experimenters (e.g. Henry Cavendish) had failed because they had tried to collect the gas over *water*.

We have already seen that on adding hydrochloric acid (i.e. a solution of hydrogen chloride in water) to zinc, hydrogen is evolved. The equation is

$$Zn + 2HCl = \underset{\text{Zinc chloride}}{ZnCl_2} + H_2$$

Many other metals act in a similar way, hydrogen being displaced and a chloride of the metal formed.

Like other acids, it causes carbonates to be decomposed, carbon dioxide being given off. Its action on calcium carbonate has already been considered. With sodium carbonate we should have

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2$$

When heated with an *oxidising agent* (i.e. a substance which will give up its oxygen to other substances), the oxygen of the oxidising agent combines with the hydrogen of the hydrochloric acid, forming water, and chlorine is set free—a gas easily recognised by its bleaching action on damp litmus, by its greenish colour and by its very characteristic pungent smell. The oxidising agent most commonly used is manganese dioxide:—

$$MnO_2 + 4HCl = 2H_2O + \underset{\text{Manganese chloride}}{MnCl_2} + Cl_2$$

Many other oxidising agents could be used instead of manganese dioxide. In fact, if we want to find out whether a substance is an oxidising agent, a good test is to heat it with hydrochloric acid and see whether chlorine is evolved.

Equations representing the action of hydrochloric acid on several other oxidising agents are given on p. 250.

Formula of Hydrogen Chloride. We shall first describe an experiment to show that one volume of hydrogen combines with one volume of chlorine to produce two volumes of hydrogen chloride. From this result we can then easily establish the formula.

The apparatus used consists of a narrow glass cylinder divided into two slightly unequal parts P and Q, which can be put into communication by means of the glass tap A. The ends are closed by ground-glass stoppers B and C.

The apparatus is first carefully dried and A is closed. The smaller part P is then filled with chlorine by displacement, while Q is similarly filled with hydrogen. The apparatus is then clamped so that P is uppermost and A is opened. The two gases rapidly mix because the heavier one is on top. The apparatus must be exposed only to *diffused* daylight because a mixture of hydrogen and chlorine explodes violently on exposure to sunlight.

After a few days the greenish colour of the chlorine will have disappeared, showing that combination has taken place. To make sure that this is complete, the apparatus is now exposed to bright sunlight. (The amount of gas still uncombined would be too small to explode.)

One end of the apparatus is now placed under mercury and the stopper is removed. None of the contained gas bubbles out and no mercury enters. This shows that the combination of the gases has taken place without change of volume.

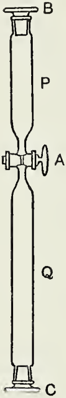


FIG. 21/4. Composition of hydrogen chloride by volume

The apparatus is next opened under water, and the latter rushes in to take the place of the hydrogen chloride. The volume which enters is found to be $2v$ c.c. where v c.c. is the volume of the smaller portion P. The gas remaining in the apparatus is easily shown to consist of hydrogen.

Clearly v c.c. of hydrogen have combined with v c.c. of chlorine, producing $2v$ c.c. of hydrogen chloride (i).

Suppose v c.c. contain n molecules of hydrogen (and therefore, by Avogadro's Hypothesis, an equal number of molecules of chlorine, or of hydrogen chloride). Instead of (i) we may write

n mols. hydrogen $+ n$ mols. chlorine give $2n$ mols. hydrogen chloride

Dividing throughout by $2n$, we have

$\frac{1}{2}$ mol. hydrogen + $\frac{1}{2}$ mol. chlorine = 1 mol. hydrogen chloride

Assuming that both a molecule of hydrogen and a molecule of chlorine contain 2 atoms, we have

1 atom hydrogen + 1 atom chlorine = 1 mol. hydrogen chloride

i.e. hydrogen chloride has the formula HCl.

Manufacture. Hydrochloric acid is obtained as a *by-product* in the manufacture of washing soda by what is known as the Leblanc process. The first stage[1] of this process consists in heating common salt with sulphuric acid. We have already seen (p. 240) that at a high temperature normal sodium sulphate, Na_2SO_4, is produced, while hydrogen chloride is given off. This sodium sulphate the manufacturer used in making his sodium carbonate. He had no use for the hydrogen chloride, so he allowed it to escape into the air.

You have no doubt noticed how very unpleasant the atmosphere of the laboratory soon becomes when a few boys are trying the effect of warming sulphuric acid with common salt. The room is soon filled with steamy, choking fumes, and everybody is coughing and making for the nearest window. Imagine the effect when common salt and acid were used by the *ton* and all the gas was allowed to escape! There was a storm of protest, and finally, in 1863, Parliament passed the Alkali Act, which compelled manufacturers to take steps to absorb these acid fumes. This was done by arranging towers filled with brick, coke, etc., and allowing water to trickle down at the same time that the gas was passing *up*. We have seen that hydrogen chloride is extremely soluble in water, so the liquid that ran out at the bottom of the towers was hydrochloric acid.

There was in those days no sale for this, so the manufacturers let it run into the nearest canal or river. It killed the fish and contaminated the water. There were more protests.

And then the situation began to clear up. In 1861 Mr Gladstone had taken the tax off paper, and the consequence was that a few years later fish ceased to be poisoned by hydrochloric acid. The explanation is very simple. When the tax was repealed paper became much cheaper. Hence far more people were able to buy newspapers, and much more paper had to be manufactured. Now the paper-making material was bleached with chlorine, and chlorine was obtained from hydrochloric acid! So the manufacturer used all his hydrochloric acid for making chlorine, and his troubles were at an end.

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[1] The Leblanc process as a whole became definitely obsolete in 1923, but the first stage of it is still carried out.

When we come to Chapter 34 on Electrolysis we shall see that by the electrolysis of brine large quantities of caustic soda (i.e. sodium hydroxide, $NaOH$) are being produced, while hydrogen and chlorine are obtained as by-products. In some works these by-products are made to combine by burning chlorine in a slight excess of hydrogen.[1] In this way 'synthetic' hydrochloric acid of a high degree of purity is made. At present about one-third of the total output of hydrochloric acid in this country is synthetic, and the proportion appears to be increasing. The rest is made by the first stage of the Leblanc process.

It is remarkable that while chlorine was formerly manufactured entirely from hydrochloric acid, hydrochloric acid should now be manufactured from chlorine.

On the large scale hydrochloric acid is usually conveyed and stored in rubber-lined tanks.

Formulæ of Chlorides. In Chapter 13 we saw that a *salt* is the substance formed when the hydrogen of an acid is replaced by a metal. If the acid is hydrochloric acid, the salt is called a *chloride*. At this point the student should read p. 42 again, in which it is explained why the formula of sodium chloride is $NaCl$, while that of magnesium chloride, for instance, is $MgCl_2$. Similarly calcium chloride would be $CaCl_2$. A very common mistake is to write such formulæ as Ca_2Cl. Remember, however, that of the two elements (in this case calcium and chlorine) you must take the *larger* number of atoms of the one which has the lower valency.

Tests for Chlorides. Nearly all chlorides, on treatment with concentrated sulphuric acid, behave in the same way as sodium chloride, i.e. they cause hydrogen chloride to be given off. The equations for sodium chloride have already been given. With calcium chloride we should have

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[1] Cf. the burning of air in an atmosphere of coal-gas (p. 227).

$$\underset{}{CaCl_2 + H_2SO_4} = \underset{\textit{Calcium sulphate}}{CaSO_4} + 2HCl$$

Hence we have an easy test for a chloride. Warm the substance with a few drops of concentrated sulphuric acid and see if hydrogen chloride is evolved. It is a gas which one soon learns to recognise.

Another test depends on the fact that though most chlorides are readily soluble, *silver chloride is insoluble in water and in nitric acid, but is soluble in ammonia.* Dissolve the suspected chloride in water and add silver nitrate solution. A white, curdy precipitate is *probably* silver chloride, showing that the original substance was a chloride. E.g.

$$NaCl + AgNO_3 = \underset{\textit{Silver chloride}}{AgCl} + \underset{\substack{\textit{Sodium nitrate} \\ \text{(which remains} \\ \text{in solution)}}}{NaNO_3}$$

To make quite sure, divide the contents of the test-tube into two parts. To one, add dilute nitric acid, and to the other add ammonia solution. If the precipitate is silver chloride, it will be unaffected by the nitric acid but will readily dissolve in the ammonia.

Still another test consists in mixing the suspected chloride with manganese dioxide and sulphuric acid, and warming. If a chloride is present, chlorine will be evolved. The sulphuric acid first acts on the chloride, giving hydrochloric acid, and the latter is then oxidised to chlorine by the manganese dioxide.

Questions

N.B. *See note in italics*, p. 132.

1. Starting from common salt, describe the preparation in the laboratory of a solution of hydrochloric acid. Draw a diagram of the apparatus you would use. Write equations *only* (in words or symbols) to represent the changes which take place when hydrochloric acid reacts with (*a*) calcium carbonate; (*b*) copper oxide; (*c*) zinc. *Camb.*

2. What weight of hydrogen chloride would be produced by heating 11·7 gm. of sodium chloride with excess of sulphuric acid? What volume would this gas occupy at 15° C. and 75 cm. pressure?

3. How would you show that hydrogen chloride is very soluble in water?

4. How would you prove that hydrogen chloride contains hydrogen?

5. Describe an experiment by which it may be shown that one volume of hydrogen combines with one volume of chlorine to form two volumes of hydrogen chloride. What law is illustrated by this result? Show that, taken in conjunction with Avogadro's hypothesis, the experiment gives information about the molecule of hydrogen and that of chlorine.

6. Calculate the percentage composition (by weight) of hydrogen chloride.

7. What volume of oxygen (calculated at N.T.P.) may be obtained by heating 4·9 gm. of potassium chlorate fairly strongly until decomposition is complete? What would be the weight and chemical nature of the residue? How would the reaction be affected if some manganese dioxide were previously mixed with the chlorate?

What would be evolved if a little concentrated sulphuric acid were warmed with (*a*) the residue after the chlorate alone had been decomposed, and (*b*) the residue after the mixture of chlorate and dioxide had ceased to give oxygen? Give equations where possible. *Lond.*

8. Describe *two* tests for a chloride, giving equations to represent the reactions that take place.

9. 2 gm. of a mixture of sodium chloride and sodium nitrate are weighed out and dissolved in water. Excess of silver nitrate is added, and the precipitate of silver chloride, after being filtered off, washed and dried, is found to weigh 2·87 gm. Find the percentage of sodium chloride in the mixture.

CHAPTER 22

CHLORINE

We have already seen that chlorine is produced on warming hydrochloric acid with an oxidising agent, the one usually employed being manganese dioxide. The equation (with an added note) was given on p. 242, but is repeated here for convenience:—

$$MnO_2 + 4HCl = 2H_2O + MnCl_2 + Cl_2$$

The apparatus usually employed is shown in fig. 22/1, the flask containing manganese dioxide[1] covered with concentrated hydrochloric acid.

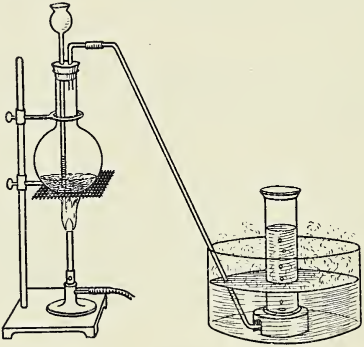

Fig. 22/1. Preparation of chlorine

All gases are less soluble in hot water than in cold, and some gases which are too soluble to be collected over cold water can be collected over hot. Chlorine is one of them (others are nitrous oxide, p. 344, and hydrogen sulphide, p. 345). It is still less soluble if the hot water has previously been saturated with common salt.

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[1] Before heating, the manganese dioxide should be well mixed with the acid or a cracked flask may result owing to impeded convection; if *granulated* manganese dioxide is used, the mixing is not so necessary.

The gas as it leaves the flask contains a certain amount of hydrogen chloride, but owing to its great solubility this impurity is removed by the hot water.

If *pure, dry* chlorine is required, the gas must be collected by displacing air upwards.

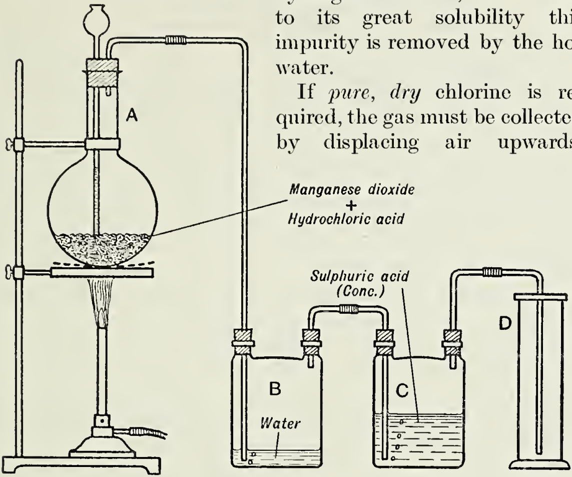

FIG. 22/2. Preparation of pure dry chlorine

In this case the impurity (hydrogen chloride) would be removed by passing the gas through a little water, and the chlorine would then be dried by passing it through sulphuric acid, or through a tube containing calcium chloride. The apparatus is shown in fig. 22/2.

Chlorine from Sodium Chloride. Instead of using hydrochloric acid in preparing chlorine, we could have used *the materials from which this acid is made*, i.e. a chloride *plus* sulphuric acid (slightly diluted, see p. 240). In practice we should use sodium chloride. Thus our flask would contain a mixture of manganese dioxide, sodium chloride and slightly diluted sulphuric acid.

Other Oxidising Agents. Instead of using manganese dioxide, we may employ other oxidising agents, e.g. red lead,

lead dioxide or potassium permanganate. The equations are:—

$$\underset{\text{Red Lead}}{Pb_3O_4} + 8HCl = 4H_2O + 3PbCl_2 + Cl_2$$

$$\underset{\text{Lead dioxide}}{PbO_2} + 4HCl = 2H_2O + PbCl_2 + Cl_2$$

$$[KMnO_4 + 8HCl = 4H_2O + KCl + MnCl_2 + 5Cl]$$
$$2KMnO_4 + 16HCl = 8H_2O + 2KCl + 2MnCl_2 + 5Cl_2$$

The key to the construction of all these equations (and also to the manganese dioxide equation on p. 248) is very simple—*take enough hydrogen* (in the hydrochloric acid) *to combine with all the oxygen of the oxidising agent.* E.g. as there are *four* atoms of oxygen in Pb_3O_4, we must have *eight* atoms of hydrogen, so we take 8HCl.

The potassium permanganate equation is not nearly so hard as it looks—if you take care to remember the formula of the permanganate. We have $KMnO_4$, so we start with 8HCl as already explained. Our hydrogen and oxygen are accounted for as $4H_2O$. It seems reasonable to expect potassium and manganese to form their chlorides, so we get KCl and $MnCl_2$ (manganese, like most metals, being divalent; cf. p. 42). We are then left with 5Cl. Lastly, we 'double all through' to get $5Cl_2$.

This reaction with potassium permanganate is one of the most convenient for the preparation of chlorine. The action takes place readily without the action of heat, and it is not even necessary to use concentrated acid. It is convenient to add the acid by means of a dropping funnel (cf. fig. 18/1).

The same remarks apply when bleaching powder is used. The equation in this case is

$$CaOCl_2 + 2HCl = CaCl_2 + H_2O + Cl_2$$

Industrial Methods. On an industrial scale, several methods have been used for the conversion of hydrogen chloride into chlorine. Formerly it was heated with manganese dioxide as in the laboratory method just described.

In 1870, however, a Mr. Henry Deacon invented a process in which manganese dioxide was dispensed with altogether.

It occurred to him that it might be possible to use the cheapest of all oxidising agents, namely, the oxygen of the air.

$$[2HCl + O = H_2O + Cl_2]$$
$$4HCl + O_2 = 2H_2O + 2Cl_2$$

Now when a mixture of hydrogen chloride and air is passed through a hot tube, only a very little of the hydrogen chloride is converted into chlorine. If, however, a suitable *catalyst* (p. 145) is employed, the yield of chlorine is increased to about 60 per cent. of the possible.[1] Deacon used a catalyst known as *cupric chloride* ($CuCl_2$), and he found that the best temperature was about 450° C. The chlorine thus obtained contains a quantity of unchanged hydrogen chloride, as well as much nitrogen from the air, and some unchanged oxygen. The hydrogen chloride is dissolved out by means of water, and the chlorine is then turned into bleaching power (p. 255).

Chlorine, however, is no longer obtained from hydrochloric acid, but by the electrolysis of brine, a process of which some account will be given on p. 416. The annual world output is about 300,000 tons!

Properties. Chlorine is a greenish-coloured gas (hence its name, Greek *chloros*=green). It has a very characteristic pungent smell, and is rather easily soluble in water. It is about $2\frac{1}{2}$ times as heavy as air, and is easily liquefied; at 0° C. a pressure of less than four atmospheres is sufficient. Liquid chlorine is employed chiefly for bleaching the cellulose pulp used in the manufacture of paper.

Just as oxygen combines with many other elements, forming oxides, so chlorine combines with them, forming *chlorides*. In some cases it is not even necessary to heat the element. Phosphorus, for instance, if put into a deflagrating spoon and lowered into a jar of chlorine, takes fire of itself, forming phosphorus trichloride and phosphorus pentachloride (PCl_3 and PCl_5). Dutch metal will likewise take fire, forming copper chloride, $CuCl_2$, mixed with some zinc chloride, $ZnCl_2$. Dutch metal looks like gold-leaf. It contains 80 per cent. of copper and 20 per cent. of zinc, and no doubt the action is so vigorous because of the large area exposed.

---

[1] Far short of 100 per cent. because the action is *reversible*. In fact, by passing a mixture of chlorine and steam over the heated catalyst oxygen can be obtained. (Cf. p. 97 foll.)

In most cases it is necessary first to heat the other element. Thus sodium, if previously ignited, burns with great brilliance, forming sodium chloride. It seems strange that sodium, an element that would take fire if you put it in your mouth, and chlorine, an extremely poisonous gas, should combine to form a compound which (after purification) you might safely take with your breakfast egg. It is a good example of the fact that the properties of a chemical compound are usually very different from those of its constituents.

The combination of chlorine with hydrogen is very important. If a flame of hydrogen is plunged into a jar of chlorine, its colour changes at once to a sickly grey, and it continues to burn freely, forming fumes of hydrogen chloride:—

$$[H + Cl = HCl] \qquad H_2 + Cl_2 = 2HCl$$

A mixture of equal volumes of hydrogen and chlorine will explode if exposed to bright sunlight, or to the light from burning magnesium ribbon, hydrogen chloride being formed in both cases.

Many of the chemical properties of chlorine are easily understood if we once thoroughly grasp this idea of its strong affinity for hydrogen. Thus

(i) A taper burns in chlorine with a red, smoky flame, producing a great deal of soot. Now the wax of a taper, like that of a candle, consists of a mixture of numerous *hydrocarbons*, i.e. compounds of hydrogen and carbon. The chlorine combines with the hydrogen, leaving the carbon, which accounts for the smoke and soot. The soot particles act as obstacles to the waves of light coming from the flame, and cause all but the longest ones (i.e. those which produce the sensation of *red*) to be turned back.

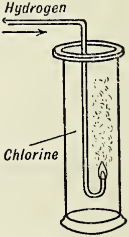

FIG. 22/3
Hydrogen burning in chlorine

(ii) A filter-paper dipped in hot turpentine takes fire (producing much soot) if plunged into a jar of chlorine. The explanation is the same as that already given, turpentine being a hydrocarbon having the formula $C_{10}H_{16}$:—

$$C_{10}H_{16}+8Cl_2=16HCl+10C$$

Incidentally, the fact that in this case and the preceding one, soot is produced in the presence of chlorine, is a reminder that chlorine does *not* react with free carbon. Similarly, it does not bleach printer's ink.

(iii) If a jar of hydrogen sulphide is placed mouth to mouth with one of chlorine, a cloud of sulphur is quickly formed:—

$$H_2S+Cl_2=2HCl+S$$

(iv) With ammonia, *nitrogen* is set free

$$[NH_3+3Cl=3HCl+N]$$
$$2NH_3+3Cl_2=6HCl+N_2$$

The hydrogen chloride so produced combines with more ammonia, forming ammonium chloride:—

$$NH_3+HCl=NH_4Cl$$

This reaction of chlorine with ammonia has its uses. You may at some time have the misfortune to get a bad sniff of chlorine—and horribly painful it is. The chlorine quickly destroys the mucous membrane, i.e. the delicate lining which covers the inside of the mouth and nose, and the fine air-passages of the lungs. If you are quick, you can prevent much of the damage (and the pain which follows it) by taking a few cautious sniffs at the ammonia bottle. The final result is that instead of containing chlorine, the air-passages contain harmless nitrogen and a little ammonium chloride, a substance not much unlike common salt.

(v) Remembering the affinity of chlorine for hydrogen, we should not be surprised to find that chlorine reacts with *water*, combining with hydrogen to form hydrochloric acid, and liberating oxygen. This is actually the case. If 'chlorine water' (i.e. a solution of chlorine in water) is exposed to sunlight, bubbles of oxygen are given off, and the solution is found to contain hydrochloric acid.

It seems that, in the first place, a mixture of hydrochloric and *hypochlorous* acids is produced:—

$$H_2O+Cl_2 \rightleftarrows HCl + \underset{\textit{Hypochlorous acid}}{HClO}$$

We have used the special sign to indicate that the reaction is decidedly of the reversible type discussed on pp. 97–101.

In the present case, however, the 'right to left' reaction is subject to a serious disadvantage, for hypochlorous acid is very unstable, breaking up in accordance with the equation $2HClO = 2HCl + O_2$. Since the hypochlorous acid is in this way gradually removed from the field of action, it is evidently only a matter of time before the 'left to right' reaction will go to completion.

The final result is, therefore, that hydrochloric acid only is left, and oxygen is given off.

One of the most remarkable properties of chlorine is its bleaching power. Flower petals, bits of coloured paper or cloth, writing ink, litmus, etc., are all bleached, *but never when moisture is carefully excluded.* Probably chlorine acts first upon the water present, forming hypochlorous acid, which then decomposes, liberating oxygen (as described above); and it is the oxygen that does the bleaching.

This explanation at once raises the question why substances are not bleached by the *air*. It looks as if a boy starting off to school in a navy-blue suit should arrive there in a white one.

We must remember, however, that oxygen usually consists of molecules containing two atoms. We suppose that when the oxygen is liberated in the course of a chemical change, the separate, single atoms of oxygen are in a great hurry to combine with *something.* Usually they combine with one another, i.e. $O + O = O_2$. If, however, vegetable colouring matter happens to be present, they combine with this colouring matter instead, turning it into some other substance richer in oxygen. Now most substances are white. Hence the new substance formed by the oxidation of the colouring matter will in most cases be white, i.e. the coloured substance will have been bleached.

This very active, 'single-atom' oxygen is said to be *nascent.* We have already met with the term in connection with hydrogen (p. 115).

To return to the subject of chlorine. All the properties so far discussed may be summed up under two heads:—

(i) Its tendency to combine with all sorts of elements forming chlorides, and in particular

(ii) Its tendency to combine with hydrogen.

There are two other properties we will mention here.

(iii) It displaces bromine from a solution of a bromide, e.g.

$$[KBr + Cl = KCl + Br] \qquad 2KBr + Cl_2 = 2KCl + Br_2$$

Similarly it displaces iodine from a solution of an iodide.

(iv) As already mentioned (p. 198), it combines with 'unsaturated' hydrocarbons. Thus with ethylene it forms an oily liquid called ethylene dichloride ($C_2H_4 + Cl_2 = C_2H_4Cl_2$).

Its reaction with carbon monoxide (p. 189) is somewhat similar.

Bleaching Powder. Almost from the time of its discovery chlorine has been used as a bleaching agent. At first the gas was simply dissolved in water, and the workmen had to dip the coloured material in the solution. Thus they were constantly exposed to the poisonous fumes. In 1799, however, a new method was adopted. The chlorine was absorbed by slaked lime,[1] thus forming 'chloride of lime' or 'bleaching powder':—

$$Ca(OH)_2 + Cl_2 = CaOCl_2 + H_2O$$

Now bleaching powder is readily decomposed by any dilute acid, chlorine being evolved (it has already been mentioned that this reaction provides us with a convenient means of preparing chlorine in the laboratory).

$$CaOCl_2 + H_2SO_4 = CaSO_4 + H_2O + Cl_2$$
$$CaOCl_2 + 2HCl = CaCl_2 + H_2O + Cl_2$$

The complete process of bleaching cotton cloth is illustrated in fig. 22/4, where six baths are represented. In no. 1 the cloth is washed by passing through a hot alkaline solution, excess of alkali being neutralised in the acid bath, no. 2. In no. 3 the cloth is saturated with water containing bleaching powder. This reacts with weak acid in no. 4 (equations just given), causing chlorine to be set free within the tubular fibres of the cloth, very thorough bleaching being the result. No. 5

---

[1] The process may easily be illustrated in the laboratory. It is only necessary to add about 30 gm. of freshly slaked lime to a jar of chlorine, and shake up thoroughly.

contains an *antichlor* to react with excess chlorine, which would cause the fabric to rot. One such antichlor is sodium thiosulphate (the 'hypo' of the photographer). The equation is not a very easy one:—

$$\underset{}{Cl_2} + \underset{\textit{Sodium thiosulphate}}{2Na_2S_2O_3} = 2NaCl + \underset{\textit{Sodium tetrathionate}}{Na_2S_4O_6}$$

In no. 6 the cloth is thoroughly washed, after which it is dried and ironed.

Before the discovery of chlorine, the bleaching process took about four months. It now takes only a few hours.

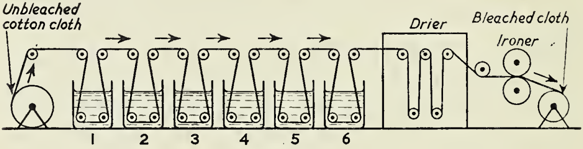

Fig. 22/4

From "Chemistry in Action," by Rawlins & Struble.
By courtesy of the publishers D. C. Heath & Co.

Bleaching powder is decomposed by the carbon dioxide and moisture present in the atmosphere:—

$$2CaOCl_2 + CO_2 + H_2O = CaCO_3 + CaCl_2 + 2HClO$$

($HClO$–hypochlorous acid. It is the steady production of this substance which gives bleaching powder its peculiar smell.)

Bleaching powder warmed with cobalt nitrate solution (which acts as a catalyst) gives *oxygen*. Thus it can be used as a source of oxygen, of chlorine and of hypochlorous acid.

Potassium Chlorate. When chlorine is passed into a *cold* solution of caustic potash the following reaction takes place:—

$$2KOH + Cl_2 = KCl + KClO + H_2O \qquad \text{(i)}$$

$KClO$ stands for *potassium hypochlorite*,[1] a very unstable substance. On heating the solution, the much more stable substances potassium chloride and potassium chlorate are produced:—

---

[1] Sodium hypochlorite solution is similarly produced from chlorine and caustic soda. Under various 'patent' names it has a wide sale as a general disinfectant, and for certain laundry purposes (bleaching effect, removal of stains, etc.).

$$3KClO = 2KCl + KClO_3 \qquad \text{(ii)}$$

If, therefore, we pass chlorine into a *hot* solution of caustic potash,[1] any hypochlorite formed is at once decomposed into chloride and chlorate. To obtain the equation representing the final result, we multiply (i) by 3, so as to obtain the '3KClO,' which is decomposed in (ii). Thus we have

$$6KOH + 3Cl_2 = 3KCl + 3KClO + 3H_2O$$
$$3KClO = 2KCl + KClO_3$$

Adding these 'partial equations,' as they are called, and cancelling the 3KClO which appears on both sides, we have

$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O$$

When the solution is concentrated by evaporation and cooled down, potassium chlorate crystallises out. This method can be made to give good results in the laboratory, but is no longer used on a manufacturing scale. An electrolytic method is used instead. The potassium chloride remains in solution because at low temperatures it is much more soluble than the chlorate.

We have already seen that potassium chlorate is used in the laboratory in the preparation of oxygen (p. 144). 'Chlorate lozenges,' which people suck when they have a sore throat, also consist of this substance. Potassium chlorate is chiefly used, however, in connection with the manufacture of matches. We shall consider the chemical action when we read about Phosphorus in Chapter 31.

Other Uses of Chlorine. Chlorine is employed in many other processes besides that of bleaching. One of these is *detinning*. The 'tins' in which so many goods are packed nowadays are made of iron with a very thin coating of tin—a somewhat costly metal. By the action of chlorine this is converted into stannic chloride ($SnCl_4$), which may either be used in the dyeing industry or converted into metallic tin.

---

[1] Practical details are given on pp. 132–4 of the author's *School Course of Practical Chemistry* (Bell).

Another use for chlorine is in the preparation of non-inflammable solvents, e.g. carbon tetrachloride (CCl_4), much used in dry-cleaning processes.

Chlorine, too, is used in sterilising drinking water—i.e. killing the bacteria which may be the cause of disease. During both Great Wars the death-rate from typhoid was remarkably low, and chlorine (usually in the form of bleaching-powder) played a great part in securing this result. Most large towns now chlorinate their water supply at a cost which may be as low as one shilling per million gallons treated. Further, the disinfection of the water of swimming-baths by means of chlorine has now become almost universal. A modern procedure is 'super-chlorination,' i.e. to make sure of killing the bacteria, three or four times the calculated minimum amount of chlorine is used. The excess is then removed by the addition of sulphur dioxide (another 'antichlor'). The equation is given on p. 283.

History. Chlorine was discovered in 1774 by a Swedish chemist named Scheele. He had served his time to an apothecary, and when he was not actually employed in serving pills and plasters over the counter he spent his time in chemical research. In spite of great drawbacks, such as lack of time, of money and of apparatus, he discovered a great many new substances. It was when he was making an examination of manganese dioxide that he discovered chlorine. 'I took a retort containing a mixture of manganese and *acidum salis*,' he says. 'In front of the neck I bound a bladder emptied of air, and set the retort in hot sand. The bladder became distended by the effervescence in the retort.' A little later he gives a very clear description of the properties of this newly discovered gas.

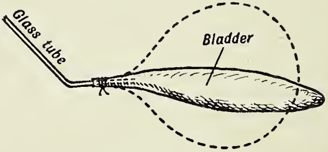

FIG. 22/5
How Scheele collected chlorine

Scheele lived in the days of the phlogistic theory, and he believed that the 'manganese' (i.e. manganese dioxide) had attracted phlogiston from the hydrochloric acid ('acidum salis' or 'marine acid,' as he calls it elsewhere). Thus, his new gas was 'marine acid' minus phlogiston, and so he gave it the name 'dephlogisticated marine acid.'

If we remember that phlogiston was roughly equivalent to our hydrogen, and that marine acid was hydrogen chloride, we see that Scheele was really quite right.

Later on, chemists went astray. Since chlorine was produced when hydrochloric acid was heated with manganese dioxide (known to be rich in oxygen), they concluded that it was a compound of oxygen and hydrochloric acid, and so they called it *oxymuriatic acid* (muriatic acid being still another name for hydrochloric acid). It was Sir Humphry Davy, in 1810, who proved that chlorine was an element.

It will be convenient here to conclude our little account of Scheele. He had discovered oxygen at least as early as 1773, i.e. a year before its independent discovery by Priestley (p. 143). Through various delays, however, the account of his work was not printed until some time after the publication of Priestley's results.

Unfortunately, Scheele worked too hard and overtaxed his strength. Many of his experiments were carried out at night in a cold and draughty shed at some distance from his shop, and it was probably these harsh conditions which brought about his death in 1786, at the early age of forty-four.

Questions

N.B. *See note in italics*, p. 132

1. Sketch an apparatus and name the substances required to prepare chlorine gas. Show how these substances react to produce chlorine. Give equations for the reaction of chlorine gas on (*a*) one metal element, (*b*) one non-metal element, and (*c*) one alkali. *Dur.*

2. How would you prepare some jars of pure, dry chlorine from common salt?

How is chlorine used to manufacture (*a*) hydrochloric acid, and (*b*) bleaching powder?

Describe the action of chlorine on aqueous solutions of (*c*) sodium iodide, and (*b*) hydrogen sulphide. *Lond.*

3. Describe and give a sketch of the apparatus which you would use to prepare a few gas-jars of chlorine from bleaching-powder.

Compare the behaviour with hydrogen of chlorine, bromine and iodine respectively.

Under what conditions and with what results does chlorine react with (*a*) ammonia, and (*b*) caustic potash? *Dur.*

4. Make a sketch of the apparatus used to prepare and collect dry chlorine. State what occurs in each part of the apparatus.

(*a*) How would you show experimentally the change that takes place when chlorine is passed into a solution of sulphur dioxide in water?

(*b*) Describe what you see when chlorine reacts with (i) hot turpentine, formula $C_{10}H_{16}$; (ii) ferrous chloride solution, and give equations for the reactions. *Scot. L.C.*

5. Describe the preparation and collection of chlorine.

How does chlorine react with (*a*) hydrogen; (*b*) slaked lime; (*c*) moist litmus paper? *O.C.*

6. Draw a labelled diagram of the apparatus you would use to produce from hydrochloric acid some jars of pure, dry chlorine. Give the equation for the reaction.

What reactions occur between chlorine and (*a*) a solution of potassium iodide; (*b*) a cold solution of caustic soda; (*c*) red-hot iron; (*d*) a burning candle? *Lond.*

7. Give the reactions that occur when a mixture of hydrogen chloride and air is passed over a suitable heated catalyst and the resulting gas is then cooled and passed over dry slaked lime. *Lond.* (*part*)

8. A good specimen of bleaching-powder would contain about 38 per cent. of 'available chlorine' (i.e. chlorine that is liberated by the action of a dilute acid). Is this what you would expect from the formula $CaOCl_2$?

9. Find the simplest formula of a substance which has the following percentage composition: potassium 24·7, manganese 34·8, oxygen 40·5. Name the substance, and mention a case in which it acts as an oxidising agent.

10. Assuming that in the process of electrolysis the whole of the chlorine is liberated from a solution of sodium chloride, what weight of the solid substance would be required for the production of 1 ton of chlorine? What weight of sodium hydroxide would be produced at the same time?

11. Sketch and label, *without* further description, an apparatus for preparing chlorine free from hydrogen chloride and passing it into a hot solution of potassium hydroxide.

Write the equation for the action. What would you observe on cooling the solution after saturation with chlorine? How would you identify the substance so obtained? *Oxf.*

CHAPTER 23

OTHER HALOGEN ELEMENTS

If the eighty or ninety children of a village were all assembled in the village hall and we observed them carefully, we should soon find that in some cases there was between one child and another a considerable resemblance. This resemblance we call a 'family likeness.' If we had many opportunities of observing all the children closely—colour of hair and eyes, shape of face, etc.—we might be able to divide them up into families, though no doubt we should make many mistakes.

The chemical elements are rather like these eighty or ninety children, for between some of them there is a remarkable family likeness. One of these families consists of the four elements, fluorine, chlorine, bromine and iodine. They are called the *halogens*, or *halogen elements*. 'Halogen' comes from two Greek words meaning 'to produce sea-salt' and this name was given to the family because certain of their compounds are present in sea-water.

Sea-water is roughly a 3 per cent. solution of a mixture of salts, largely sodium chloride (which accounts for rather more than three-quarters of the total). The remainder is composed chiefly of magnesium chloride and sulphate, calcium sulphate and potassium chloride. *Bromides* are present in very small proportions (and *iodides* smaller still), but as we shall see presently, they serve as a very important source of bromine.

Fluorine is a very interesting element, but its study lies outside the scope of this book. Chlorine formed the subject of our last chapter. We shall now deal briefly with bromine and iodine, dwelling more particularly on those properties which show that they really do belong to the same family of elements.

Physical Properties. This family likeness is not very evident on a casual inspection of the elements, except that the smell both of bromine and iodine rather reminds one of chlorine. If, however, we set out the chief physical properties

CHLORINE, BROMINE AND

Element	*Atomic weight*	*State at ordinary temp.*	*Sp. gr. of liquid*	*Colour*	*Melting-point*	*Boiling-point*	*Solubility at 0° C. (gm. per litre)*
Chlorine	35·5	Gas	1·55	Green	−101° C.	−34° C.	14·7
Bromine	80	Liquid	3·19	Reddish brown	−7° C.	59° C.	47·1 [1]
Iodine	127	Solid	4·9 (solid)	Black (solid), Purple (vapour)	113° C.	184° C.	0·19

---

[1] Bromine does not occupy its usual intermediate position.

[2] HBr is more easily decomposed by heat than HCl, and HI than HBr. Note also that Cl displaces Br from its compounds with metals, and with hydrogen (e.g. it displaces Br from KBr). Similarly Br displaces I. But [*proceed to Note* 3 *on opposite page*],

in tabular form (as shown above), we are much struck with one point. The properties of bromine seem to be a sort of rough 'average' of the properties of chlorine and iodine. We can easily illustrate this statement by noting the atomic weights, melting-points, boiling-points and specific gravities. In each case the value for bromine lies between the values for chlorine and iodine respectively. This intermediate position of bromine will often be noticed in connection with the chemical properties of the halogens, which we must now consider.

Chemical Properties. The resemblance between chlorine, bromine and iodine is seen in a large number of their chemical properties, thus

(1) Bromine and iodine, like chlorine, are *univalent* and form bromides and iodides corresponding to the chlorides. For instance, corresponding to potassium chloride KCl, we have potassium bromide KBr and iodide KI. Lead forms a chloride, $PbCl_2$, a bromide, $PbBr_2$, and an iodide, PbI_2; similarly for many other elements.

These compounds often show a close resemblance in properties. Thus potassium chloride, bromide and iodide all crystallise in cubes. The lead salts are all comparatively

IODINE COMPARED

Valency	*Condition for combining with hydrogen*	*Properties of hydrogen compounds* [2]	*Oxides* [3]	*Silver compounds*	*Potassium compounds*
Generally 1. (Compounds, HCl, HBr, HI; AgCl, AgBr, AgI, etc.)	Light Combine with increasing difficulty ↓	Similar composition (HCl, HBr, HI). Gases which fume strongly in moist air. All extremely soluble in water, giving strongly acid solutions.	Forms very unstable oxides	AgCl. White. Easily sol. in ammonia All insol. in water and in nitric acid	KCl. Sol. in water All crystallise in cubes
	Heat		Several rather unstable oxides	AgBr. Pale yellow. Slightly sol. in ammonia	KBr. More sol.
	Heat + Catalyst		Forms stable oxides	AgI. Strong yellow. Insol. in ammonia	KI. Still more sol.

[3] In compounds with *oxygen*, displacement is in the opposite direction. Thus iodine will displace chlorine from potassium chlorate: $2KClO_3 + I_2 = 2KIO_3 + Cl_2$.

insoluble in cold water and much more soluble in hot, so that they readily crystallise out when a hot solution is cooled. The silver salts are all insoluble in water and nitric acid. Silver chloride is readily soluble in ammonia, the iodide is insoluble, while the bromide is moderately soluble. In colour also the bromide occupies an intermediate position, for silver chloride is white, and silver iodide is a well-defined yellow; silver bromide is a very pale yellow.[1]

The most striking resemblances are seen in the compounds with *hydrogen*, HCl, HBr and HI. These are all gases which 'steam' in moist air, and all are extremely soluble in water, forming acid solutions.

As we pass from chlorine to iodine these compounds with hydrogen are formed less and less readily. Thus chlorine and hydrogen combine with explosive violence when merely exposed to sunlight. Bromine and hydrogen require the application of heat, while iodine and hydrogen require not simply heat, but also the presence of a catalyst; and even then the combination is not complete.

---

[1] Such facts as are contained in this paragraph are quickly verified in the laboratory, and are then easy to remember. To 'learn' them, apart from practical observation, would be a sheer abuse of memory.

(2) If chlorine is passed through a solution of bromide (e.g. potassium bromide), bromide is at once liberated:—

$$2KBr + Cl_2 = 2KCl + Br_2$$

It also liberates iodine from an iodide. Similarly, bromine liberates iodine from an iodide:—

$$2KI + Br_2 = 2KBr + I_2$$

(To show this, add bromine water to potassium-iodide solution containing a little starch. The latter is at once turned blue by the liberated iodine.)

(3) Chlorine, bromine and iodine are liberated from their compounds by similar methods.

To liberate chlorine from a *chloride*, we heat it with manganese dioxide and sulphuric acid. The reaction is explained on p. 249. Similarly, if sulphuric acid is added to a mixture of manganese dioxide and a *bromide* we obtain bromine; if we use an *iodide* instead of the bromide we get iodine.

Preparation. (i) *Bromine.* On a commercial scale, bromine is prepared as indicated in paragraph (2) above, i.e. by the action of chlorine on a bromide. Until recently, the necessary bromides were derived exclusively from certain natural deposits, chiefly at Stassfurt in Germany, but sea-water is now the main source of supply. This contains bromides, mainly of sodium and magnesium, and the essential part of the process is the displacement of bromine from these bromides by means of chlorine. The dilution is so great, however, that some 2,000 gallons of sea-water have to be treated in order to yield a single pound of bromine.

There is a very large plant operating at Freeport in Texas, but the process is now being worked on the coast of Cornwall and also of Anglesey; and some thousands of tons of bromine are being produced annually in this country. About two-thirds of the output is used for combining with ethylene, forming the dibromide $C_2H_4Br_2$. This (together with the chloride, $C_2H_4Cl_2$) is used as a solvent for lead tetraethyl, $Pb(C_2H_5)_4$. The latter compound when added to petrol reduces 'knocking', but leaves a deposit of lead or lead oxide, which damages the ignition points. In the presence of ethylene bromide, however, lead bromide is formed, which at the existing high temperature vaporises and is carried off.

In 1949 we imported nearly a quarter of a million pounds of bromine. All this has stopped, and we now export it.

In the laboratory, bromine is not usually prepared by the displacing action of chlorine, but by the method indicated in fig. 23/1. The retort contains a mixture of potassium bromide and manganese dioxide, which is heated with *slightly* diluted sulphuric acid (2 vols. acid poured into 1 vol. water). The bromine vapour readily condenses in the stem of the retort, and the liquid drops into the flask.

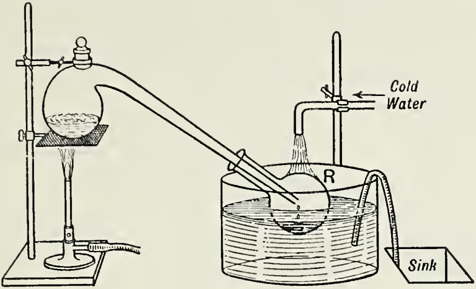

FIG. 23/1. Preparation of bromine

(ii) *Iodine.* Most of the world's supplies are obtained from the nitrate deposits of Chile (p. 332), which contain a small proportion of iodine present as sodium iodate, $NaIO_3$ (cf. potassium chlorate, $KClO_3$). The average iodine content is about 1½ parts per thousand. As much as possible of the sodium nitrate is removed by treatment with water and crystallising out, after which the final mother liquors are found to contain from 10 to 20 gm. of sodium iodate per litre. From this solution, iodine is precipitated by the addition of sodium bisulphite, $NaHSO_3$.

In the laboratory we may use the apparatus of fig. 23/2, but with a mixture containing potassium iodide instead of bromide. Much of the iodine lodges in the neck of the retort, but can be driven forward into the flask by gently heating.

Hydrogen Compounds. Suppose we take three test-tubes and place in them a little potassium chloride, bromide and iodide respectively. Now let us add a little concentrated sulphuric acid to each, and heat.

We find:—

(i) In the first, steamy fumes of hydrogen chloride are freely evolved, but there is evidently *no chlorine*, for litmus remains unbleached.

(ii) In the second, the steamy fumes (hydrogen bromide) are not quite so pronounced, but the brown vapour of *bromine* is easily observed.

(iii) In the third, it is only by close observation that we can see any steamy fumes at all (hydrogen iodide). *Iodine*, however, is freely produced, and there is the unmistakable 'bad-egg' smell of hydrogen sulphide.

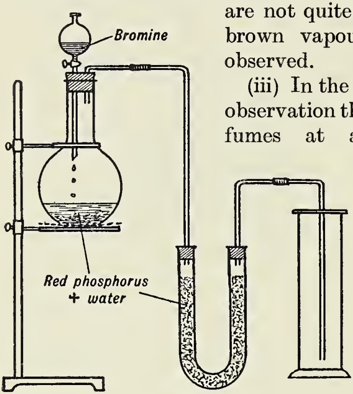

FIG. 23/2
Preparation of hydrogen bromide

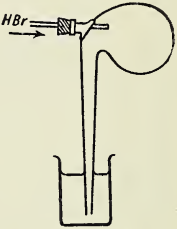

FIG. 23/3
Making a solution of hydrogen bromide

How are we to explain these results?

The first reaction has already been discussed and is represented by the equation

$$KCl + H_2SO_4 = KHSO_4 + HCl$$

Hydrogen chloride is a very *stable* substance (i.e. it shows little tendency to decompose under the action of heat), so there the reaction ends.

The second reaction is similar up to a certain point:—

$$KBr + H_2SO_4 = KHSO_4 + HBr$$

Hydrogen bromide, however, is not very stable, and its tendency to break up is assisted by the fact that hot concentrated sulphuric acid acts as a mild oxidising agent. Thus we get

$$H_2O{\cdot}SO_3 + \frac{HBr}{HBr} = H_2O + SO_2 + H_2O + Br_2$$

or $$H_2SO_4 + 2HBr = 2H_2O + SO_2 + Br_2$$

Hydrogen iodide is still less stable, so although it is produced in the first instance:—

$$KI + H_2SO_4 = KHSO_4 + HI$$

it is almost completely oxidised to iodine:—

$$H_2SO_4 + 8HI = H_2S + 4H_2O + 4I_2$$

It will now be evident that we can *not* conveniently prepare hydrogen bromide by a method similar to that used for hydrogen chloride (p. 240). The product would be mixed with sulphur dioxide and bromine, impurities which it would be very difficult to remove.

The method used depends on the fact that phosphorus tribromide, PBr_3, and phosphorus pentabromide, PBr_5, are decomposed by water according to the equations

$$PBr_3 + 3H_2O = \underset{\text{Phosphorous acid}}{H_3PO_3} + 3HBr$$

$$PBr_5 + 4H_2O = \underset{\text{Phosphoric acid}}{H_3PO_4} + 5HBr$$

Red phosphorus (7 gm.) mixed with water (14 c.c.) is placed in a flask fitted with a dropping funnel containing bromine (14 c.c.). The latter is allowed to fall, drop by drop, into the flask, and there is a rather vigorous action, the heat produced being sufficient to vaporise a considerable amount of the bromine. This bromine vapour is removed by means of the U-tube, which contains broken glass smeared with a mixture of water and red phosphorus. The hydrogen bromide issuing from the U-tube is collected by displacing air upwards in the usual way. If a *solution* of the gas is required, some such device as that shown in the figure must be adopted to prevent 'sucking back.'

When all the bromine has been added, the flask may be heated to expel some of the dissolved hydrogen bromide. Except for this, there is no need to apply heat.

The phosphorus and bromine react according to the equations

$$2P + 3Br_2 = 2PBr_3 \quad \text{and} \quad 2P + 5Br_2 = 2PBr_5$$

and the tri- and pentabromide are then decomposed in accordance with the equations already given.

Hydrogen iodide may be prepared by a very similar method, but in this case the iodine and phosphorus are placed in the flask, and water is run in from the dropping funnel.

A solution of hydrogen iodide (i.e. hydriodic acid) soon goes brown on exposure to the air, owing to liberation of iodine:—

$$[2HI + O = H_2O + I_2] \qquad 4HI + O_2 = 2H_2O + 2I_2$$

Hydrochloric acid under the same circumstances does *not* produce chlorine. This is another illustration of a fact we have already noted—that hydrogen iodide is much more easily oxidised than hydrogen chloride. As we should expect, hydrogen bromide occupies an intermediate position—bromine is liberated when its solution is exposed to the air, but sunlight is necessary, and even then the oxidation is not so rapid as in the case of hydriodic acid.

Uses. Bromine itself is not much used outside the chemical laboratory, but ethylene dibromide, as already mentioned, is largely used in the petrol industry. Potassium bromide and iodide are employed in medicine and photography.

Tincture of iodine consists of an alcoholic solution of iodine (iodine, $\frac{1}{2}$ oz., potassium iodide, $\frac{1}{4}$ oz., rectified spirit, 1 pint), and is much used to prevent wounds from becoming septic.

Iodine is present in the human body (and the bodies of other animals), chiefly in the thyroid gland in the neck. This gland contains not free iodine, but a rather complex substance called thyroxin, in which iodine is present to the extent of 65 per cent. Goitre (or 'Derbyshire neck') and some diseases of a much more serious character have been traced to defects of the thyroid gland, and have been treated very successfully by giving doses of iodine, usually in the form of potassium iodide and iodate. It is said that under modern conditions our bodies often fail to obtain sufficient iodine from the food we eat, and so 'iodised table salt' has come largely into use. It consists of ordinary salt to which minute quantities of sodium iodide have been added.

Questions

N.B. *See note in italics,* p. 132

1. 'The properties of bromine are often a sort of average between those of chlorine and iodine.' Illustrate.

2. State the reasons for classifying together the elements chlorine, bromine and iodine.

Describe one method in each case you would use to obtain (*a*) chlorine from sodium chloride; (*b*) bromine from potassium bromide. *Dur.*

3. Chlorine is passed into an aqueous solution of potassium iodide, and it is found that 1·7 gm. of iodine have been liberated. Calculate the volume of chlorine used at 17° C. and 770 mm. pressure. *Camb.*

4. Describe how you would prepare a sample of hydrogen bromide. How does an aqueous solution of this gas react with (*a*) zinc; (*b*) chlorine; (*c*) concentrated sulphuric acid?

O.C. Alt.

5. A small crystal is thought to be iodine. Describe two tests, either of which could be applied to verify this.

Compare the actions of chlorine and iodine on (i) water; (ii) potassium bromide solution; (iii) hydrogen.

Describe how you would prepare and collect hydrogen iodide in the laboratory. Explain why it cannot be prepared in a manner similar to that used for the preparation of hydrogen chloride.

Scot. L.C.

6. 2 gm. of a mixture of potassium bromide and potassium chlorate are weighed out and dissolved in water. Excess of silver nitrate solution is added, and the precipitate of silver bromide is filtered off. After being washed and dried this is found to weigh 1·88 gm. Find the percentage of potassium bromide in the original mixture.

7. Assuming that by treatment with suitable quantities of water and red phosphorus, 6 gm. of bromine are completely converted into hydrogen bromide, what volume of the latter gas would be obtained if measured at 12° C. and 74·6 cm. pressure?

CHAPTER 24

SULPHUR

Sulphur occurs in the free condition in various parts of the world, especially in the vicinity of volcanoes. For many years it was obtained almost exclusively from the slopes of Mount Etna in Sicily, but it will be seen from fig. 24/1 that, usually, about 90 per cent. of the world's supply now comes from the United States (chiefly Texas).

In Texas the sulphur, mixed with limestone, occurs in beds 30–40 yards in thickness at a depth of 700 or 800 feet below the surface. A hole is drilled to reach this sulphur-bearing limestone, and through it three concentric pipes are passed, usually of 6 inches, 3 inches and 1 inch diameter. Water at about 170°–180° C. is sent down the outer pipe (the water is raised to a temperature much above its normal boiling-point by increasing the pressure). A study of the diagram will show how this water enters the sulphur-bearing limestone. Though not so hot as it was, it is still well above the melting-point of sulphur (112·8° C.). The latter is therefore melted out, and being heavier than water it forms a pool below. The water pressure above it drives it (mixed with some water) inside the pipe system, and almost at once up the

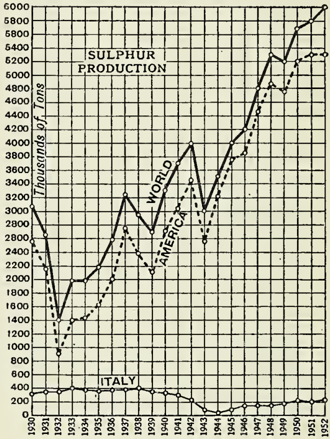

Fig. 24/1 [1]

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[1] Figures from *Minerals Year Book* (U.S. Bureau of Mines).

annular space between the two inner pipes, but this pressure is not great enough to drive it to the surface. The extra pressure is obtained by forcing compressed air down the 1-inch pipe, and a frothy mixture of sulphur, water and air completes the ascent and empties into an immense vat, where the sulphur quickly solidifies. It is very pure—usually over 99·8 per cent.—and requires no further treatment.

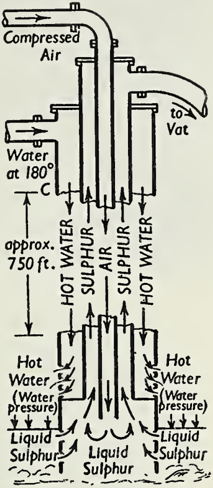


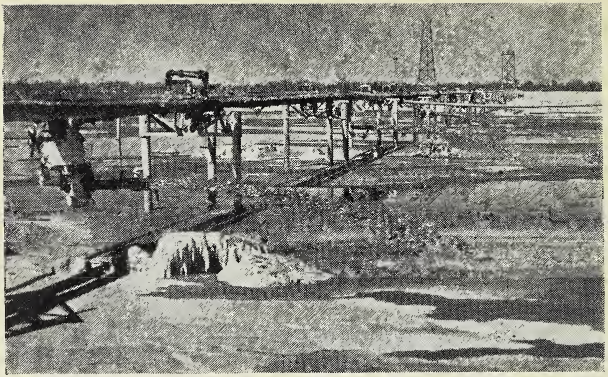
FIG. 24/2

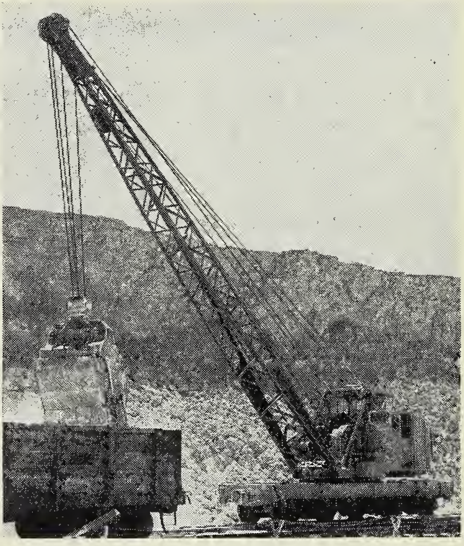
Some of the vats are $\frac{1}{4}$ mile long and over 50 feet deep. After removal of the containing walls, the solid mass is drilled and blasted to facilitate removal (lower illustration, p. 272). A modern sulphur well will yield about 6000 tons of sulphur a day for three or four months, after which a new shaft has to be sunk.

Behaviour on Heating. When sulphur is heated in a test-tube, it first melts (at 112·8°) to a limpid, amber-coloured liquid. The colour darkens as the temperature is raised, until at the boiling-point (444° C.) it is nearly black.

At the same time, some curious changes take place in the *viscosity of* the liquid (i.e. in the ease with which it flows; a 'thick' liquid like treacle is said to be 'viscous,' while a 'thin' one is said to be 'limpid'). Very limpid when first melted, the sulphur rather suddenly becomes viscous, and at about 180° will scarcely run out of the test-tube. After that it becomes less and less viscous as it is heated, though it never quite regains its former limpidity.

If soon after being melted it is poured into water, it at once assumes a 'granulated' form as we should expect, but it is not otherwise different from the sulphur we started with. If, however, we heat it beyond the very viscous stage and *then* pour it into water, we obtain 'plastic sulphur,' which will stretch almost like india-rubber. A still better arrangement





By courtesy of Texas Gulf Sulphur Co.

Above. Molten sulphur discharging into vat
Below. Loading sulphur into waggon from face of vat

is that indicated in fig. 24/3. Plastic sulphur is not a true solid at all. It is what is known as a 'super-cooled liquid.' After a few days it is found to have turned into ordinary sulphur, brittle and with a crystalline structure.

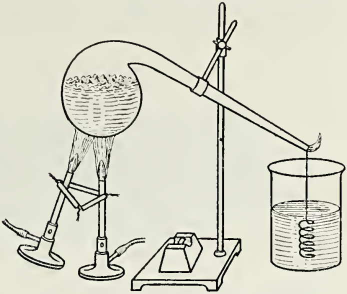


FIG. 24/3. Making plastic sulphur

Allotropic Forms of Sulphur. Sulphur occurs in a large number of allotropic forms, of which we shall consider four.

(i) *Rhombic sulphur* is the most stable form at ordinary temperatures, and the other forms which we shall mention all become rhombic after being left for a while. A rhombic crystal of very simple shape is shown in fig. 24/4. This crystal has eight faces, and so rhombic sulphur is often known as *octahedral sulphur.*

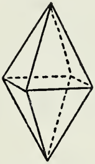


FIG. 24/4
Crystal of rhombic sulphur

Roll sulphur and flowers of sulphur both consist mainly of octahedral crystals, but the latter are very small and imperfect. To obtain good crystals, some flowers of sulphur should be shaken up with three or four times its volume of carbon disulphide. Most of it dissolves, and the clear solution is poured on to a clock-glass and left in a fume cupboard to evaporate. In this way very beautiful crystals may be obtained.

(ii) *Monoclinic sulphur* is obtained by melting some sulphur in an evaporating dish. It is allowed to cool until a crust *just* forms on the surface. Two small holes are made in this, and the still liquid portion is poured out from beneath. On cutting out the crust, it is found to present an appearance something like that shown in fig. 24/5. The crystals are apparently needle-shaped, but really consist of very thin, long prisms. After a few days it is found that they become opaque, and that each one of them now consists of a large number of minute *rhombic* crystals. The sulphur has gone back to its more usual form. Monoclinic sulphur is sometimes known as *prismatic* sulphur.

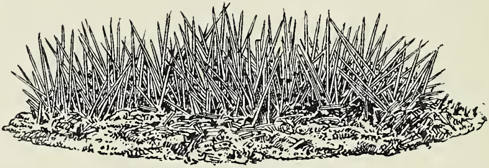


FIG. 24/5. Prismatic sulphur

The gradual change from the prismatic to the rhombic form can be recognised by the colour, for prismatic sulphur is of a paler yellow colour than rhombic.

(iii) *Plastic sulphur* has already been mentioned. Its non-crystalline form is no doubt due to the fact that, owing to the sudden cooling, the molecules had not time to arrange themselves in the regular order which is necessary for the formation of crystals.

(iv) *Amorphous sulphur.* There are really several forms of amorphous sulphur (including, of course, plastic sulphur), but the name is usually reserved for a form which occurs to the extent of about 30 per cent. in flowers of sulphur. When the latter is shaken up with carbon disulphide the 'rhombic' portion dissolves, as already mentioned. On filtering, a fine white powder remains behind on the filter-paper. This is 'amorphous sulphur.'

Rhombic and monoclinic sulphur are both soluble in carbon disulphide, while plastic and amorphous sulphur are both insoluble. The four forms also differ somewhat in density, melting-point and in various other ways, as shown in the table on the opposite page.

Identity of the Various Forms. Why are we sure that rhombic sulphur, plastic sulphur, etc., really are the same element in different forms? The question is easily answered by experiment.

	Rhombic	*Prismatic*	*Plastic*	*Amorphous*
Appearance, etc.	Yellow octahedral crystals; brittle	Pale yellow needle-shaped crystals; brittle	Amber coloured amorphous substance; stretches like rubber	Pale yellow amorphous powder
Sp. gr.	2·06	1·96	1·92	2·05
M.P.	112·8° C.	119·3	114·5	120
Solubility in CS_2	Soluble	Soluble	Insoluble	Insoluble
Stability	At ordinary temperatures rhombic sulphur is the only stable form; all other forms revert to this.			

Suppose we prepare a small quantity of any one of the allotropic forms of sulphur—say prismatic sulphur—and weigh it. On leaving it for a week or so, we can show (by examination with a lens) that it has turned back to rhombic sulphur, but *there is no change of weight.* Thus, although there has been a change of *form*, there has been no change of *substance.*

Uses. Large quantities of sulphur are used in the manufacture of sulphuric acid. Very often, however, instead of using sulphur itself for this purpose, certain compounds of sulphur known as *sulphides* are employed, as is also calcium *sulphate*, $CaSO_4$ ('anhydrite').

Sulphur is also much used for manufacturing a compound known as *calcium bisulphite*, which is required for turning wood into wood-pulp—a half-way stage in the manufacture of paper. Sulphur is also employed in hop gardens and vineyards to prevent certain diseases in the plants.

As part of the compound antimony sulphide, sulphur is largely used in the manufacture of safety matches. It has many minor uses, e.g. as a medicine, and in the manufacture of gunpowder.

We must not omit to mention, however, that sulphur is largely used for 'vulcanising' rubber. Crude rubber is sticky[1] and of very little use. In 1839 a man named Goodyear found that by heating rubber with sulphur it lost its stickiness and could be used for scores of purposes. The proportion of sulphur varies from about 4 up to 30 per cent., the higher proportions being used when harder varieties of rubber such as ebonite and vulcanite are required.

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[1] A sticky area on bunsen tubing, produced by accidental contact with a flame, may usually be 'dried' by rubbing it with flowers of sulphur.

Questions

1. Give *three* important natural sources of sulphur. Why is sulphur such an important raw material? *Oxf.* (*part*)

2. A naturally occurring compound which serves as an important source of sulphur for industry, has the percentage composition: calcium, 29·4, sulphur 23·5, oxygen 47·1. Find its simplest formula, and give (i) its chemical name; (ii) the name by which it is known in industry. [Ca = 40; S = 32; O = 16.]

3. Describe *one* method by which sulphur is obtained from natural sources. *Camb.* (*part*)

4. Describe the changes that take place when sulphur is heated gradually until it boils. What happens when melted sulphur is poured into cold water, the melted substance being (i) just above its melting point; (ii) just below its boiling point?

5. Describe, with full experimental details, how you would obtain, from flowers of sulphur, specimens of the four main allotropic forms of this element. *Camb.* (*part*)

6. With the help of the Index, make as full a list as you can of elements that exist in allotropic forms, mentioning the various forms (e.g. plastic sulphur). Which seem to show the greater tendency to occur in allotropic forms, metals or non-metals?

7. How would you show that the various allotropic forms of sulphur are really the same element?

8. Give *three* uses of sulphur in everyday life. *Lond.* (*part*)

CHAPTER 25

SULPHUR DIOXIDE

Preparation. (i) We have already seen (p. 150) that sulphur dioxide may be obtained by burning sulphur, contained in a deflagrating spoon, in a jar of oxygen:—

$$S + O_2 = SO_2$$

Air may be used, but in that case the gas will be mixed with a large quantity of nitrogen.

(ii) The usual laboratory method is to heat copper turnings with concentrated sulphuric acid, the gas being collected by displacing air upwards (fig. 25/1)

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2$$

Copper sulphate, water and sulphur dioxide are actually formed, so that the equation tells the truth —but it does not tell the whole truth. When the reaction is over, it is always found that the flask contains a large quantity of greyish-black, insoluble material, which has been found to consist of cuprous sulphide, Cu_2S. Evidently other changes take place besides that represented by the equation.

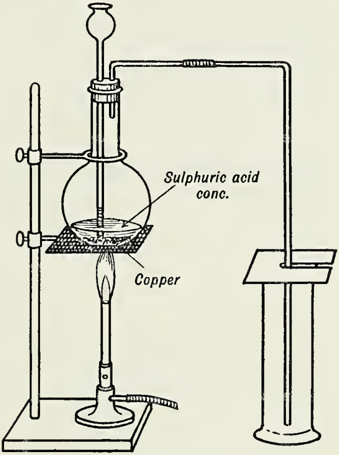

Fig. 25/1
Preparation of sulphur dioxide

It seems curious that the presence of copper sulphate in the flask does not cause the liquid residue to be *blue*. Copper sulphate is blue, however, only when combined with 'water of crystallisation' (its formula then being $CuSO_4 \cdot 5H_2O$). Without this water it is *white*, and so a crystal of blue vitriol goes white when heated, or after being left for some time in concentrated sulphuric acid, which withdraws its water of crystallisation. In the experiment we are discussing, the small amount of water available is secured by the concentrated acid, and the sediment in the flask would be white but for the presence of the cuprous sulphide already mentioned.

On pouring the sediment into a large quantity of water, a blue solution is obtained.

To obtain a good specimen of crystallised copper sulphate, pour this solution back into the flask. Boil up for a few minutes (to complete the process of extraction) and filter. On cooling, the filtrate deposits crystals. Pour off the mother liquor, wash the crystals with a *little* water and then let them drain and dry on a piece of clean blotting-paper.

(iii) If only two or three gas-jars are required, a much easier and safer method is to put a handful of sodium sulphite crystals in a flask and cover them with dilute hydrochloric or sulphuric acid. On warming, the gas is readily evolved. The method will be understood better after p. 281 has been read.

$$\underset{\textit{Sodium sulphite}}{Na_2SO_3} + 2HCl = \underset{\textit{Sodium chloride}}{2NaCl} + H_2O + SO_2$$

Reduction and Reducing Agents. On p. 114 we saw that reduction means loss of oxygen. We must now go more fully into the meaning of this term, because otherwise we cannot get a very clear idea of the properties of sulphur dioxide.

When we come to the chapter on Electrolysis we shall find that oxygen appears at the *positive* terminal or anode. It is therefore said to be an *electro-negative* element (a positively charged body attracts a negatively charged one). Hydrogen always appears at the *negative* terminal or cathode, and is therefore said to be *electro-positive*. Water, then, is a compound of an electro-positive element (hydrogen) and an electro-negative one (oxygen).

In many cases we can regard other compounds as being built up in the same way. In sodium chloride, for instance, the electro-positive element is sodium and the electro-negative one is chlorine. Speaking generally, hydrogen and the metals are electro-positive, while oxygen and the non-metals are electro-negative. Specially important electro-negative elements (besides oxygen) are chlorine and sulphur. The 'acidic' groups CO_3, SO_4, NO_3, etc. (in carbonates, sulphates, nitrates, etc.) are also electro-negative.

The term reduction, which at one time was used to mean simply loss of oxygen, may now mean the loss of *any* electro-negative element or group. Thus we speak of ferric chloride, $FeCl_3$, being reduced to ferrous chloride, $FeCl_2$; mercuric nitrate, $Hg(NO_3)_2$, being reduced to mercurous nitrate, $HgNO_3$, and so on. Further, the term is now used to include not simply the loss of an electro-negative element, but also the *gain* of an *electro-positive* one. Thus chlorine may be reduced to hydrogen chloride (gaining the electro-positive element hydrogen); cupric oxide, CuO, may be reduced to cuprous oxide, Cu_2O; and so on. Summing up these various ideas, we may define ***reduction*** as *a chemical change involving either* (i) *loss of oxygen or other electro-negative element* (*or group*), *or* (ii) *gain of hydrogen or other electro-positive element.*

A ***reducing agent*** has already been defined as *a substance which brings about reduction.*

On p. 114 we considered the chemical change

$$\text{Copper oxide} + \text{Hydrogen} = \text{Copper} + \text{Water}$$

or

$$CuO + H_2 = Cu + H_2O$$

and we noticed that the *reduction* of the copper oxide is accompanied by the *oxidation* of the hydrogen. We may take this as an example of the general rule that *oxidation is accompanied by reduction.*

This will be a convenient point at which to define ***oxidation.*** It is simply the opposite to reduction, and so may be defined as *a chemical change involving either* (i) *gain of oxygen or other electro-negative element* (*or group*), *or* (ii) *loss of hydrogen or other electro-positive element.*

Before leaving the subject, we must consider one or two cases that may be found rather puzzling.

(1) *Loss of the elements of water is neither oxidation nor reduction.* Thus sulphurous acid is extremely unstable, and breaks up readily into sulphur dioxide and water ($H_2SO_3 = H_2O + SO_2$). The sulphurous acid has certainly lost oxygen, but then it has also lost an equivalent amount of hydrogen.

(2) We speak of the reduction of sulphuric acid to sulphur dioxide. Why? Sulphuric acid may be regarded as $H_2O \cdot SO_3$. To become sulphur oxide, it must lose (i) the elements of water, which is neither oxidation nor reduction, and (ii) oxygen ($SO_3 \rightarrow SO_2$). This loss of oxygen, of course, makes the case one of reduction.

Similarly we speak of nitric acid being reduced to nitrogen dioxide, NO_2, or nitric oxide, NO. We may think of nitric acid, HNO_3, as $H_2O \cdot N_2O_5$. The student can see the rest for himself.

After this rather long digression we can now proceed to the

Properties of Sulphur Dioxide. The gas is colourless and has a characteristic, choking smell of burning sulphur. It has also a characteristic taste, very perceptible when it is being prepared in the laboratory and a little has escaped into the air.

One sometimes notices this taste during foggy weather in a town. No doubt the gas dissolves in the minute droplets of water of which the fog consists, and in this way is kept close to the ground instead of escaping freely into the atmosphere.

Sulphur dioxide is extremely soluble in water, and is much heavier than air. It is on account of these two properties that it is collected by displacing air upwards. It is easily liquefied. The gas may be passed into a wide test-tube, as shown in the figure, the test-tube being surrounded with a freezing mixture of ice and salt.

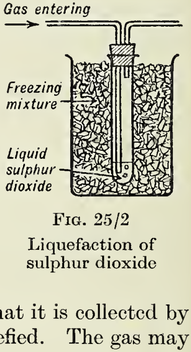

FIG. 25/2

Liquefaction of sulphur dioxide

On taking out the test-tube and inserting a thermometer, the sulphur dioxide will be found to boil at $-9°$ C. Liquid sulphur dioxide can be bought in stout glass syphons.

Although the temperature of the room may be 15° or 20° C. the liquid does not boil, because of the pressure of the gas above it. On p. 270 we had another example of the fact that the boiling-point of a liquid is raised when the pressure is increased.

Sulphur dioxide does not burn nor support combustion. Its solution in water turns litmus red owing to the formation of *sulphurous acid* ($SO_2 + H_2O = H_2SO_3$). As already mentioned, this acid is very unstable. Much of it decomposes even at ordinary temperatures into water and sulphur dioxide, but (with access of air) some of it is slowly oxidised to sulphuric acid.

We should expect an acid to be neutralised by a basic oxide, with the formation of a salt and water (p. 151). Thus, sulphurous acid is neutralised by calcium oxide (quicklime):—

$$CaO + H_2SO_3 = \underset{\textit{Calcium sulphite}}{CaSO_3} + H_2O$$

In practice it is more convenient to use calcium carbonate (chalk):—

$$CaCO_3 + H_2SO_3 = CaSO_3 + H_2O + CO_2$$

If sodium oxide (Na_2O) were used we should obtain sodium sulphite. In practice we always use sodium hydroxide, NaOH, which we may regard as $Na_2O \cdot H_2O$:—

$$2NaOH + H_2SO_3 = \underset{\textit{Sodium sulphite}}{Na_2SO_3} + 2H_2O$$

Thus, if sulphur dioxide is passed into a solution of sodium hydroxide, a neutral solution is obtained after a while, and from this, after removing some of the water by evaporation, we may obtain crystals of sodium sulphite.

If we continue to pass sulphur dioxide through a solution of sodium sulphite, sodium *bisulphite* is obtained:—

$$Na_2SO_3 + H_2O + SO_2 = 2NaHSO_3$$

Compare this change with the action of carbon dioxide on sodium carbonate and on calcium carbonate (p. 178).

When a sulphite is warmed with dilute hydrochloric or sulphuric acid, sulphur dioxide is readily evolved, e.g.

$$CaSO_3 + 2HCl = CaCl_2 + H_2O + SO_2$$

This may be compared with the action of hydrochloric acid on calcium carbonate:—

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

We have already seen that in the action of hydrochloric acid on sodium sulphite we have a convenient means of preparing sulphur dioxide.

We must just notice the compound *potassium metabisulphite*, $K_2S_2O_5$ or $K_2SO_3.SO_2$, sold in tablet form for bottling fruit. When the bottles and contents are heated, sulphur dioxide is given off, and this kills the germs which would cause putrefaction.

Before proceeding further, let us glance over some of the formulæ we have been using.

Calcium is divalent (i.e. will replace *two* atoms of hydrogen), while sodium is univalent (i.e. will replace only *one*). Thus to replace two atoms of hydrogen (in H_2SO_3) we require *two* atoms of sodium but only *one* of calcium. Hence we have sodium sulphite, Na_2SO_3, and calcium sulphite, $CaSO_3$.

Note the termination *-ous* in sulphurous acid. This termination, in an acid, is used when another acid exists with a higher proportion of oxygen. The latter acid is the *-ic* acid. Thus we have sulphur*ous* acid, H_2SO_3, and sulphur*ic* acid, H_2SO_4. We call H_2CO_3 carbon*ic* acid (not carbon*ous* acid) because no acid exists having the formula H_2CO_4.

The salts derived from *-ous* acids are *-ites*, while those derived from *-ic* acids are *-ates*. Thus from sulphurous acid we derive the sulphites, and from sulphuric acid the sulphates. Later on we shall meet with nitric acid and nitrous acid, giving rise to nitrates and nitrites respectively.

Sulphurous acid, H_2SO_3, shows a strong tendency to take oxygen from other bodies, becoming sulphuric acid, H_2SO_4; i.e. it is a *reducing agent*. Thus if a solution of potassium permanganate is shaken up with sulphurous acid (or with sulphur dioxide) the rich purple colour is at once discharged. Let us see why this is a case of reduction.

Potassium permanganate has the formula $KMnO_4$, and the colourless solution is found on examination to contain manganous sulphate, $MnSO_4$, and potassium sulphate, K_2SO_4.

We may regard each of these salts as a compound of two oxides. We will write potassium permanganate as $K_2O + Mn_2O_7$ ($= 2KMnO_4$), manganous sulphate as $MnO + SO_3$, and potassium sulphate as $K_2O + SO_3$. So

$(K_2O + Mn_2O_7) + SO_2$ becomes $(K_2O + SO_3) + (MnO + SO_3)$.[1]

We see now that

(i) Potassium remains at the same stage of oxidation
(ii) Mn_2O_7 must have *lost* oxygen to become MnO
(iii) SO_2 ,, ,, *gained* ,, ,, ,, SO_3

In short, the potassium permanganate has been reduced and the sulphur dioxide has been oxidised.

In your laboratory work with sulphur dioxide you are sure to have found that it causes a solution of potassium chromate to turn from yellow to green. Potassium chromate is K_2CrO_4 ($= K_2O{\cdot}CrO_3$). The green solution contains potassium sulphate, K_2SO_4 ($= K_2O{\cdot}SO_3$), and chromium sulphate, $Cr_2(SO_4)_3$ ($= Cr_2O_3{\cdot}3SO_3$). It will be a good exercise for you to show that this is another example of reduction. The 'working out' is very similar to the case of potassium permanganate already dealt with.

In the next chapter we shall see that sulphurous acid will reduce the brown gas nitrogen dioxide, NO_2, to the colourless one, nitric oxide ($H_2SO_3 + NO_2 = H_2SO_4 + NO$). This reaction is the basis of the 'lead chamber' process for the manufacture of sulphuric acid.

On p. 256 we saw that sodium thiosulphate is sometimes used as an *antichlor*, i.e. a substance for removing the last traces of chlorine from fabrics which have been bleached with that gas. Sulphur dioxide may also be used for this purpose. The bleached fabric is steeped in a solution of the gas, when any chlorine is removed according to the equation

$$\boxed{Cl_2 + H_2}\;\boxed{O + H_2SO_3} = 2HCl + H_2SO_4$$

i.e.
$$Cl_2 + 2H_2O + SO_2 = 2HCl + H_2SO_4$$

Here the chlorine has been reduced, having gained the electro-positive element hydrogen.

---

[1] The two sides do not balance, but the statement serves to indicate the general nature of the change. The *equation* might be written
$(K_2O + Mn_2O_7) + 5SO_2 + 2H_2O = (K_2O + SO_3) + 2(MnO + SO_3) + 2H_2SO_4$

Sulphur dioxide is a *bleaching agent.* Rose petals, magenta dye and other substances soon lose their colour when exposed to the moist gas. It seems likely that sulphurous acid acts upon water, forming sulphuric acid and liberating nascent hydrogen:—

$$H_2SO_3 + H_2O = H_2SO_4 + 2H$$

(2H is written here instead of H_2, to indicate that the hydrogen exists in the form of single atoms). This nascent hydrogen, being very active, readily combines with oxygen in the colouring matter, leaving a white substance. Thus the coloured substance becomes white by loss of oxygen, i.e. by reduction (contrast bleaching by chlorine, which is due to loss of hydrogen, i.e. to oxidation, p. 254).

It is probable that in many cases of bleaching by sulphur dioxide the explanation just given would require some modification, but a full discussion of the subject would take us rather too far afield.

On the large scale, sulphur dioxide is used for bleaching certain substances, such as straw, wool and silk, which would be injured if treated with the more usual bleaching agent (chlorine). A serious drawback is that such bleaching is often only temporary. Everybody has noticed how straw hats and flannels gradually resume their original yellow colour.

We have now had a good number of cases in which sulphur dioxide has acted as a reducing agent. It is rather surprising to find that, in at least one instance, it can act as an *oxidising agent*! If a jar of sulphur dioxide is placed mouth downwards in contact with a jar of hydrogen sulphide, a yellow cloud of sulphur is at once produced:—

$$SO_2 + 2H_2S = 2H_2O + 3S$$

Clearly the hydrogen sulphide has lost hydrogen and has therefore been oxidised.

There is another point of interest about this reaction. Both sulphur dioxide and hydrogen sulphide are present in the gases emitted from volcanoes, and some of the sulphur always found in such districts may have been formed in accordance with the equation just given.

Proof of Formula. On p. 175 we considered an experiment in which the formula of carbon dioxide was proved to be CO_2. Using sulphur instead of carbon, we can carry out the same experiment to establish the formula of sulphur dioxide.

Historical Note. Sulphur dioxide is one of the many gases which were first investigated by Priestley. He had been heating hydrochloric acid, and had succeeded in obtaining a gas, much too soluble to be collected over water, but which he was able to collect over mercury. It struck him that he might obtain another gas if he heated *sulphuric* acid instead of hydrochloric acid. In the course of the experiment a little mercury was accidentally drawn back into the hot sulphuric acid, and sulphur dioxide at once began to come off:—

$$Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2$$

Except that we use copper instead of mercury, Priestley's method is still the one usually employed for preparing the gas in the laboratory.

Questions

N.B. *See note in italics*, p. 132

1. Describe how you would prepare several jars full of sulphur dioxide. How does this gas react with (*a*) moist litmus paper; (*b*) caustic soda? *O.C.* (*part*)

2. To prepare sulphur dioxide, copper turnings have been heated for some time in a flask with concentrated sulphuric acid. Describe and explain the appearance of the residue in the flask. How could you obtain from it a crystalline specimen of copper sulphate, $CuSO_4 \cdot 5H_2O$?

3. Make out a table of four columns headed respectively (i) Reducing agent; (ii) Example of reaction; (iii) Reduction product; (iv) Oxidation product. In column (i) enter the four reducing agents Hydrogen, Carbon, Carbon monoxide, Sulphur dioxide, and complete the table. Column (ii) should include the equation representing the reaction.

4. Compare and contrast carbon dioxide and sulphur dioxide.

5. How would you prepare a specimen of sodium sulphite? What happens when this substance is warmed with dilute hydrochloric acid?

6. Describe and explain what happens when sulphur dioxide is passed into a solution of sodium hydroxide until it is saturated. *Camb.* (*part*)

7. 'Bleaching is accompanied by either oxidation or reduction.' Justify this statement by reference to *two* gases which act as bleaching agents, specifying the methods and the materials you would use to demonstrate their bleaching action.

Describe the preparation of *one* of these gases. How is bleaching-powder made? *Lond.*

8. Sulphur dioxide is passed for some time into water contained in a test-tube. Hydrogen sulphide is afterwards passed into the solution so formed. Describe what you would expect to see. Name the products and write the equation representing the reaction.

9. Describe a method for the liquefaction of sulphur dioxide. How would you show that the element sulphur is present in sulphur dioxide and that the gas contains its own volume of oxygen? *J.M.B.*

10. A syphon contains 3 lb. of liquid sulphur dioxide. How many litres of gas measured at N.T.P. would this furnish? (1 lb. = 454 gm.)

11. What weight of sulphur dioxide would be produced by burning 16 gm. of sulphur, and what volume would the sulphur dioxide occupy (i) at N.T.P.; (ii) at 15° C. and 72 cm. pressure?

12. Enough sulphur is burnt in 284 c.c. of oxygen to convert the latter completely into sulphur dioxide. Find the volume of the sulphur dioxide if measured at the same temperature and pressure as the original oxygen.

CHAPTER 26

SULPHURIC ACID

If sulphur dioxide and oxygen are mixed together, no change takes place. If, however, the mixture is passed over finely divided platinum, combination takes place, a substance consisting of white silky crystals being formed. It is called *sulphur trioxide*:—

$$[SO_2 + O = SO_3]$$
$$2SO_2 + O_2 = 2SO_3$$

In the laboratory the experiment is usually carried out as follows:

Sulphur dioxide from a syphon, and oxygen from a cylinder, are passed into a bottle, A, containing concentrated sulphuric acid. This acid eagerly absorbs moisture, and so after passing through it the gases are dry. Further, by watching the bubbles we can easily see whether each gas is being passed at a suitable speed.

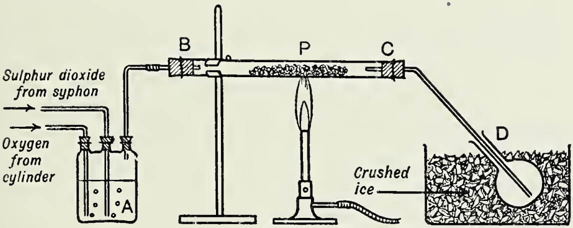

Fig. 26/1. Preparation of sulphur trioxide

The mixed gases now enter BC, a combustion-tube containing a quantity of platinised asbestos, P,[1] heated with a bunsen. Sulphur trioxide forms as thick white fumes, which are collected in the flask D surrounded with crushed ice.

---

[1] Made by soaking asbestos fibre in a solution of platinum chloride, and then drying and igniting. The platinum chloride decomposes, leaving the platinum as a finely divided residue clinging to the fibres of the asbestos.

By a slight modification of the method just described we can obtain sulphur trioxide from sulphur and oxygen. In this case oxygen alone (from the cylinder) passes first through the bottle, and then over the sulphur, which is heated in a suitable tube. The sulphur dioxide so produced, together with the *excess* of oxygen, then passes over heated platinised asbestos, the rest of the apparatus being as already described.

The most striking property of sulphur trioxide is that on putting it into water a very energetic action takes place and *sulphuric acid* is produced. Sulphur trioxide is, in fact, sometimes called sulphuric anhydride:—

$$SO_3 + H_2O = H_2SO_4$$

Catalysis. At the close of the experiment the platinised asbestos is found to have undergone no permanent change; yet in its absence the sulphur dioxide and oxygen would not have combined, or at least would only have combined with extreme slowness. *A substance which alters the rate at which a chemical action proceeds, without itself undergoing any permanent change, is known as a* ***catalyst*** *or* ***catalytic agent****, and the phenomenon is known as* ***catalysis***.

We have had previous examples of catalysts. There was manganese dioxide, which when mixed with potassium chlorate caused the oxygen to come off much more readily, but was itself unchanged at the close of the experiment (p. 145). Then in Deacon's process (p. 250) we saw that by using cupric chloride as a catalyst it was possible to oxidise hydrogen chloride by means of atmospheric oxygen. Water often acts as a catalyst, as when chlorine is used for bleaching purposes. Some examples of the catalytic action of water are even more striking. It has been shown, for instance, that provided *extreme care* is taken to remove all traces of water vapour, hydrogen chloride can be mixed with ammonia without the production of the familiar dense fumes of ammonium chloride, while phosphorus can be melted and even *boiled* in an atmosphere of oxygen, without taking fire!

A great many catalysts are known. In fact, when a chemist wishes to speed up a chemical reaction, one of the first things he does is to look round for a suitable catalyst. A well-known example occurs in the manufacture of indigo. At one stage in the process it is necessary to change a substance called naphthalene into another one called phthalic anhydride. On heating with sulphuric acid the change *does* take place, but with such dismal slowness that the manufacturers were almost in despair. Then chemists set to work to find a catalyst. One of them in particular had tried substance after substance without result, and one afternoon he had the misfortune to break a thermometer with which he was stirring the mixture of naphthalene and sulphuric acid. This proved to be the darkest hour before the dawn, for in a few minutes the naphthalene had completely changed into phthalic anhydride! The mercury which came from the bulb of the thermometer had acted as a catalyst, and mercury is used to this day to catalyse that particular reaction.

Contact Process. Though the experiment just described (for the preparation of sulphur trioxide) has been known since 1831, it is only since 1901 that the method has been successfully employed on the large scale for the manufacture of sulphuric acid.

The necessary sulphur dioxide is obtained in various ways:—

(1) By the burning of sulphur imported from America.

(2) 'Spent oxide' from the gas-works, which contains about 50 per cent. of free sulphur (p. 204), may be used instead of pure sulphur.

(3) Iron pyrites or copper pyrites is often used, special furnaces called 'pyrites burners' being employed. Iron pyrites is a sulphide of iron, FeS_2. On burning it, sulphur dioxide comes off and oxide of iron is left behind (the equation is given on p. 303). Copper pyrites has the formula $CuFeS_2$, and in this case oxide of iron and oxide of copper are both left. These residues are sometimes used as sources of iron and copper.

(4) By heating *anhydrite* (calcium sulphate, $CaSO_4$) with a mixture of ashes of suitable composition and coke. The chemical changes are somewhat complicated, but will be discussed on p. 386 in connection with the manufacture of Portland cement.

There is a simple reason for the adoption of the 'anhydrite' method. About 1950 America was becoming deeply concerned about the drain on her sulphur supplies, and began to 'ration' her customers. As a result, manufacturers looked round for other means of obtaining sulphur dioxide.

Now in this country there are practically unlimited supplies of anhydrite, and notably at Billingham (Co. Durham), where the I.C.I. has important works. By treating the anhydrite in the way just mentioned, a ton of Portland cement may be made for every ton of sulphuric acid. This turns what would otherwise be a rather expensive process into a reasonably economical one.

Having mentioned the various ways of obtaining the necessary sulphur dioxide, we will now consider the 'Contact Process' in some detail, this name having been given to a process which depends on the combination of sulphur dioxide with oxygen, forming sulphur trioxide, in the presence of a catalyst.

At first, after the plant had been set up at great expense, the manufacturers were horrified to find that

(i) Only a part of the sulphur trioxide dissolved in the water (forming sulphuric acid). The remainder escaped into the air, filling the entire works with choking fumes.

(ii) After a few days the catalyst ceased to act.

On carefully examining the catalyst it was found that it contained a quantity of *arsenic*. It was easy to account for its presence. The ores (containing combined sulphur) which were burnt to produce sulphur dioxide also contained arsenic. While the sulphur was burning to form sulphur dioxide, the arsenic was forming arsenious oxide, a white powder which settled among the finely divided platinum. For some reason or other the platinum was unable to act as a catalyst when this arsenic was present. It was said to be 'poisoned.' A simple process was devised for removing the arsenious oxide before it reached the platinum, and there was afterwards no trouble on this score.

With regard to the other difficulty, it was found that if the sulphur trioxide was passed into concentrated sulphuric acid (about 98 per cent.) instead of into water, it was much more completely absorbed. We shall see in a moment how this fact is applied.

The whole process[1] is illustrated diagrammatically in fig. 26/2, but a few notes may usefully be added.

(1) '*Series of Purifiers.*' For the reason already mentioned, extreme care is taken in the matter of purification, which actually takes place in five stages. In this brief outline we cannot describe the methods employed, but it is worth noting that before the gaseous mixture enters the first of the purifiers it is seen as a thick smoke, while as it emerges from the last it is perfectly transparent.

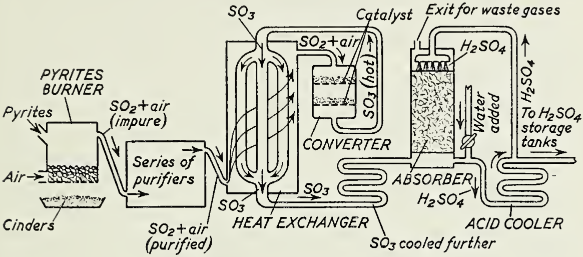

FIG. 26/2. Contact process

(2) *Converter.* Here the mixed gases pass over and through the catalyst, spread on perforated shelves. It may consist of finely divided platinum, but the modern tendency is rather to employ vanadium pentoxide, V_2O_5. In either case an inert carrier such as silica gel is employed, corresponding to the asbestos of our experiment.

(3) *Heat Exchanger.* The action in the converter is exothermic (i.e. heat is given out), and the sulphur trioxide leaves at a temperature of about 560° C. This is much too hot for the next process (absorption).

On the other hand, the incoming mixture of sulphur dioxide and air needs to be fairly hot if reaction is to take place readily (about 400°–450° is aimed at in practice). In the exchanger, the mixture which needs heating passes round tubes through which the hot sulphur trioxide is moving. Thus the trioxide is cooled, while the sulphur dioxide–air mixture is heated.

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[1] For many points in the present chapter, especially such as relate to the manufacture of sulphuric acid, the writer gratefully acknowledges his indebtedness to the authors of *Sulphuric Acid*, a small book issued by Imperial Chemical Industries Ltd.

(4) *Absorber.* The absorbing liquid, consisting of sulphuric acid of about 98 per cent. strength, trickles downwards over an inert packing material such as quartz, meeting and absorbing the ascending trioxide, which combines with the 2 per cent. or so of water. The descending acid, of course, becomes stronger as a result, the conditions being adjusted so that it shall leave the tower at about 99 per cent. strength. It is brought back to 98 per cent. by the addition of water, after which some is recirculated through the absorber, while the remainder is run into storage tanks.

Lead Chamber Process. Until 1914 sulphuric acid was manufactured in England almost entirely by the 'lead chamber' process.

The process gets its name from the huge lead tanks in which the acid is made, lead being one of the few common metals which will withstand the action of the acid.

In order to obtain a general idea of the process, it will be necessary to anticipate two points from Chapter 30.

(i) When a mixture of ammonia (a gas, NH_3) and air is passed through a platinum gauze and heated to a moderate temperature, the ammonia is oxidised to a colourless gas called nitric oxide, NO

$$[2NH_3 + 5O = 2NO + 3H_2O]$$
$$4NH_3 + 5O_2 = 4NO + 6H_2O$$

(ii) Nitric oxide readily combines with oxygen, forming the brown gas nitrogen dioxide:—

$$[NO + O = NO_2]$$
$$2NO + O_2 = 2NO_2$$

The chambers are supplied with a mixture of nitrogen dioxide, water, air and sulphur dioxide. Let us first notice the source of each of these.

Nitric oxide is obtained by the oxidation of ammonia, as we have just seen. The platinum gauze acts as a catalyst.

Water is supplied as a fine spray from several jets placed in the roof of the chamber.

Sulphur dioxide is produced by one of the methods already mentioned on p. 289.

Air. Air must, of course, be supplied to the pyrites ovens for the combustion of the sulphur or sulphides. *Extra* air, however, is introduced, which mixes with the sulphur dioxide and enters the lead chambers, where it takes part in the chemical changes which will now be described.

In the lead chambers the reactions which take place are:

(i) Water, with sulphur dioxide, forms sulphurous acid:—

$$H_2O + SO_2 = H_2SO_3$$

(ii) Nitric oxide combines with oxygen (present in the air that has been introduced), forming nitrogen dioxide:—

$$2NO + O_2 = 2NO_2$$

(iii) The nitrogen dioxide reacts with sulphurous acid, forming sulphuric acid:—

$$NO_2 + H_2SO_3 = H_2SO_4 + NO$$[1]

The nitric oxide is now re-oxidised to nitrogen dioxide according to equation (ii) above, and the whole round of changes is repeated again and again.[2] The nitric oxide is said to act as a *carrier*. It is very curious that though sulphurous acid will not take up oxygen directly from the air (or at least will only take it very slowly), it will take it readily through the medium of nitric oxide.

Theoretically a given supply of nitric oxide would last for all time. In practice there is for various reasons a certain amount of wastage—not very much—and this has to be made good. (Actually, additional supplies are admitted between the Glover tower and the first lead chamber, but to avoid complication this is not shown in the diagram.) We will see now how this wastage is reduced to a minimum.

The lead chambers are usually arranged in a series of three or four, and the gas emerging from the last of them is made to pass up the *Gay-Lussac tower*. This is filled with inert stone packing—often acid-resisting bricks arranged in chequer fashion, so that there are spaces between them. Over this packing concentrated sulphuric acid trickles, and the upward current of gases meets the downward stream of acid. The valuable oxides of nitrogen dissolve in the acid, probably with chemical change.

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[1] It is now accepted that sulphurous acid is not *directly* oxidised by nitrogen dioxide to sulphuric acid. There are complicated intermediate reactions, but a knowledge of them would be expected only from an advanced student.

[2] Examination of rain, especially in manufacturing towns, often shows the presence of small quantities of sulphur dioxide and nitrogen peroxide. These, with water, furnish all the substances necessary for a huge lead-chamber process on a highly diluted scale. The sulphuric acid so produced does much damage, especially to buildings of limestone.

How are these oxides of nitrogen to be extracted so that they can be used again?

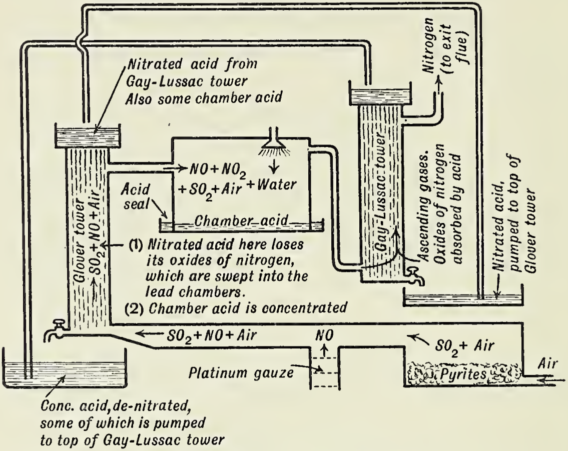
Nitrogen (to exit flue)
Nitrated acid from Gay-Lussac tower Also some chamber acid
$NO+NO_2$ $+SO_2+Air$ +Water
Acid seal
Chamber acid
Glover tower
$SO_2+NO+Air$
(1) Nitrated acid here loses its oxides of nitrogen, which are swept into the lead chambers.
(2) Chamber acid is concentrated
Gay-Lussac tower
Ascending gases. Oxides of nitrogen absorbed by acid
Nitrated acid, pumped to top of Glover tower
$SO_2+NO+Air$
NO
SO_2+ Air
Air
Platinum gauze
Pyrites
Conc. acid, de-nitrated, some of which is pumped to top of Gay-Lussac tower

FIG. 26/3. Lead chamber process

The 'nitrated acid' from the bottom of the Gay-Lussac tower is pumped to the top of the *Glover tower*, placed between the pyrites burners and the first lead chamber. As the nitrated acid trickles down this tower it meets the ascending stream of hot gases (i.e. sulphur dioxide from the pyrites burners, mixed with the excess of air of which we have already spoken, and also mixed with the nitric oxide which is always being supplied to make up for wastage). The result is that the oxides of nitrogen are expelled from the nitrated acid, afterwards passing on to the lead chambers.

Useful purposes served by the Glover tower are: (i) The 'chamber acid' (i.e. the comparatively dilute acid produced in the lead chambers) is concentrated. It is mixed with the nitrated acid already mentioned, and as it descends the Glover tower, much of the water is removed by the current of hot gases which it meets. (ii) The hot gases from the pyrites burners, etc., need to be *cooled* to 90° or so before entering the lead chamber; the descending acid needs to be *heated* (to concentrate it). Thus the Glover tower serves as a 'heat exchange.'

Diagrammatically, the arrangement may be represented as shown in fig. 26/3, but it should be mentioned that in some modern plants the lead chambers are replaced by two packed towers. These are followed by two Gay-Lussac towers, and preceded by a 'denitrating' tower (practically a Glover tower). The five towers constitute what are known as a 'Petersen' plant, and are constructed of acid-resisting masonry.

The 'chamber' product is not allowed to reach a higher concentration than 65 per cent. or so, because beyond that point it begins to attack the lead rather seriously. As explained above, further concentration—actually to about 78 per cent.—takes place in the Glover tower. It is quite possible to remove still more water, but the process is somewhat costly.

For some purposes the contact process was the best one for Germany, who needed a fairly concentrated acid for the manufacture of indigo dye, while the lead chamber process was quite suitable for England, for whose purposes (largely the manufacture of a fertilizer known as 'superphosphate') a less concentrated acid served very well. On the outbreak of war, however, in 1914, immense quantities of high explosives had to be manufactured, and for this a very concentrated acid was required. Naturally Germany did not offer to send us a supply. Hence new works to make acid by the 'contact' process began to be set up in England. It looks as if this process will gradually displace the older one. Thus in England, in 1926, 'contact' acid accounted for only 11 per cent. of the total, but by 1934 this figure had risen to 24·7, and by 1955 to 72·2.

Properties. Sulphuric acid is a colourless, heavy, oily liquid ('oil of vitriol'—it used to be prepared from 'green vitriol' or ferrous sulphate). Except when very specially purified it always contains 2–3 per cent. of water. When mixed with water great heat is produced, and this has sometimes been the cause of accidents through the acid splashing about. It is important when diluting the acid always to pour the acid into water, *not* water into the acid.

Sulphuric acid has a high boiling-point, 338° C., and this has much to do with its great capacity for bringing about chemical change, which is always much more rapid as the temperature is raised. If it had a *low* boiling-point, this increase of temperature would simply 'drive it from the field' in the form of vapour, and its chance of producing chemical change of any sort would be at an end. As it is, even when made very hot it still remains in contact with the substance we wish it to attack. Above the boiling point it begins to dissociate ($H_2SO_4 \rightleftharpoons H_2O + SO_3$) and at 450° C. dissociation is complete. The subject of dissociation will be more fully discussed on p. 350.

Sulphuric acid absorbs water greedily, i.e. it is ***hygroscopic.*** Hence it is often used in the laboratory for drying gases (we had one example on p. 287, where it was used for drying sulphur dioxide and oxygen). If a beaker half-full of the concentrated acid is put on a shelf for a week or two, it will be found that the beaker gradually fills up, owing to absorption of moisture. A small beaker of sulphuric acid is often kept inside a balance case which we wish to keep dry, and the same liquid is frequently used in a desiccator.

Sulphuric acid not only absorbs water, it also absorbs *the elements of water*, which as we saw on p. 187 is not quite the same thing. Thus cane sugar has the formula $C_{12}H_{22}O_{11}$. Sulphuric acid absorbs '$H_{22}O_{11}$' (the elements of $11H_2O$), leaving carbon, and so the sugar is *charred.* The elements of water, no longer combined with the carbon, actually unite to form water, which dilutes the acid. The explanation of the charring effect of sulphuric acid on paper, wood, etc., is quite similar.

Three cases in which sulphuric acid absorbs the elements of water have already been discussed. These are (i) oxalic acid, $H_2C_2O_4$ (p. 187) (ii) formic acid, H_2CO_2 (p. 188) and (iii) hydrated copper sulphate, $CuSO_4 \cdot 5H_2O$ (p. 277).

Action on Carbon and Sulphur. Only the hot, concentrated acid has any action, and in this case the carbon and sulphur are *oxidised* to carbon dioxide and sulphur dioxide respectively. It will help us to understand the action, if for the moment we think of sulphuric acid, H_2SO_4, as $H_2O\cdot SO_3$. By the loss of *one* atom of oxygen this would become $H_2O + SO_2$. Now if carbon is to be oxidised to carbon dioxide, *two* atoms of oxygen are required, and we therefore take *two* molecules of sulphuric acid, thus:

$$\begin{array}{l} H_2O\cdot SO_3 \\ \\ H_2O\cdot SO_3 \end{array} + C = \begin{array}{ccc} H_2O & & SO_2 \\ & + & \\ H_2O & & SO_2 \end{array} + CO_2$$

or

$$2H_2SO_4 + C = 2H_2O + 2SO_2 + CO_2$$

Similarly with sulphur we have

$$2H_2SO_4 + S = 2H_2O + 2SO_2 + SO_2$$

i.e.

$$2H_2SO_4 + S = 2H_2O + 3SO_2$$

Action on Metals. In the first instance, we may suppose that the *hot concentrated* acid oxidises the metal. Most common metals are divalent, therefore only *one* oxygen atom will be required. Thus in the case of copper

$$H_2O\cdot SO_3 + Cu = H_2O + SO_2 + CuO \quad . \quad . \quad (i)$$

Now copper oxide cannot remain unchanged in the presence of sulphuric acid. It is a basic oxide, and will form a salt and water

$$CuO + H_2SO_4 = CuSO_4 + H_2O \quad . \quad . \quad (ii)$$

Adding the two equations together and 'cancelling' CuO, which occurs on both sides, we get

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2$$

We have had this equation before (p. 277), but unless we take the trouble to work through the 'partial equations,' as (i) and (ii) are called, it is not very obvious that the action is one of oxidation.

Cold concentrated sulphuric acid is usually without action on a metal. In fact, the concentrated acid is often conveyed on railways in big cylindrical tanks made of mild steel.

Dilute sulphuric acid sometimes has no action (e.g. on copper and lead). Speaking generally, however, the metal displaces hydrogen, e.g.

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$
$$Fe + H_2SO_4 = FeSO_4 + H_2$$

The most important thing to notice is that with the hot concentrated acid the action is one of *oxidation*, while with the dilute acid it is one of *displacement*.

Sulphuric Acid is Dibasic. We learned on p. 153 that a salt is the substance produced when the hydrogen of an acid is replaced by a metal. Some acids (e.g. hydrochloric, HCl) contain only one hydrogen atom that can be displaced in this way. Sulphuric acid (H_2SO_4) contains two, and phosphoric acid (H_3PO_4) contains three. By the ***basicity of an acid*** we mean *the number of hydrogen atoms, contained in one molecule of the acid, that are replaceable by a metal.*

The student may think that the last six words are superfluous, but they are not. Acetic acid, for instance, $C_2H_4O_2$, contains four hydrogen atoms, but only one of them is replaceable by a metal. Its basicity is therefore one, not four.

To prove that sulphuric acid is dibasic we must contrive to make two distinct sodium (or potassium) salts from it, the first by replacing only one of the hydrogen atoms, the second by replacing them both. The formulæ would be $NaHSO_4$ and Na_2SO_4 respectively. We go to work as follows.

Measure out, say, 40 c.c. of caustic soda solution into each of two evaporating dishes. To one of them add a drop of litmus solution to act as indicator, and then with constant stirring run in dilute sulphuric acid from a burette until the liquid is just neutral. Suppose 30 c.c. of acid were required. Now add *twice* this amount, i.e. 60 c.c., to the caustic soda in the second dish.

Concentrate both solutions until they are strong enough to deposit crystals. Then in each case pour off the liquor, dry the crystals on blotting paper and examine them.

The substances differ in crystalline form, in solubility and in taste.[1] On heating, one of them gives off thick white acid fumes,[1] the other does not. Further, however carefully we purify them (e.g. by recrystallising again and again from hot water), one always gives an acid solution, the other a neutral one.

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[1] Further, the neutral sulphate will be tinted because of the litmus. This effect can be avoided, of course, by mixing a fresh portion (40 c.c.) of caustic soda with 30 c.c. of sulphuric acid.

The fact is that we have obtained two distinct sulphates of sodium. The equations representing their formation would be

$$\text{(i)}\ H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O$$
$$\text{(ii)}\ H_2SO_4 + NaOH = NaHSO_4 + H_2O$$

The first equation represents the reaction in which we used the litmus. Comparing the two, it will be noticed that for a given amount of caustic soda the amount of sulphuric acid in the second case is twice as great as in the first. That is why we used 60 c.c. of acid in the second dish as compared with 30 c.c. in the first.

By no change in the amount of sulphuric acid can we obtain a third sulphate, so we conclude that only two hydrogen atoms are replaceable by sodium, i.e. the acid is dibasic.

Normal Salts and Acid Salts. $NaHSO_4$ (sodium hydrogen sulphate) represents an ***acid salt***, i.e. *the substance formed when only part of the hydrogen of an acid is replaced by a metal.* If the whole of the hydrogen has been replaced, the salt is said to be ***normal.*** If no special adjective is used, the normal salt is always understood.

Note that an acid salt occupies an intermediate position between the acid itself and the normal salt:—

$$H_2SO_4 \qquad NaHSO_4 \qquad Na_2SO_4$$

This point becomes clearer, perhaps, if we write $NaHSO_4$ as $Na_2SO_4 \cdot H_2SO_4 (= 2NaHSO_4)$. The solution of an acid salt does not necessarily turn litmus red, though it often does so.

Some Important Sulphates

Sodium sulphate, $Na_2SO_4 \cdot 10H_2O$. Used in medicine as 'Glauber's salt.'

Magnesium sulphate, $MgSO_4 \cdot 7H_2O$, is used medicinally as 'Epsom salt,' so called because it was found in the water of a spring near Epsom in Surrey.

Copper sulphate, $CuSO_4 \cdot 5H_2O$ (blue vitriol); see p. 465.

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[1] Of sulphuric acid; $2NaHSO_4 = Na_2SO_4 + H_2SO_4$.

Calcium sulphate, $CaSO_4 \cdot 2H_2O$; see p. 430.

Barium sulphate, $BaSO_4$. This is notable for its high degree of insolubility, giving us a very delicate test for a sulphate.[1] We make a solution of the suspected sulphate, and add to it a solution of barium chloride, $BaCl_2$. If any sulphate is present we at once obtain a white precipitate of barium sulphate, e.g. $Na_2SO_4 + BaCl_2 = BaSO_4 + 2NaCl$. Now barium chloride forms white precipitates not only with sulphates, but also with carbonates, phosphates, etc. (the precipitates consisting of barium carbonate, barium phosphate, etc.). Barium sulphate, however, is *insoluble in hydrochloric acid.* If the precipitate does not dissolve on adding this acid, a sulphate must have been present.

Lead sulphate, $PbSO_4$. This is also very insoluble. Owing to the presence of calcium sulphate in drinking-water, a coating of lead sulphate is formed on the inside of lead pipes used to convey water. This is a good thing, for the coating separates the water from the lead, and so makes it impossible for soluble lead compounds to be formed. Soluble lead compounds are poisonous.

A good antidote in cases of lead-poisoning is magnesium sulphate, which reacts with the soluble lead compound, forming the highly insoluble (and therefore comparatively harmless) lead sulphate.

Ammonium sulphate, $(NH_4)_2SO_4$, is made in large quantities in gas-works, by neutralising a solution of ammonia with sulphuric acid:—

$$2NH_4OH + H_2SO_4 = (NH_4)_2SO_4 + 2H_2O$$

It is used as a fertilizer.

Alum. This is described on p. 440.

Other Uses. We have already referred incidentally to two important uses of sulphuric acid, in the manufacture of the fertilizers superphosphate and ammonium sulphate. It is used also in the viscose process for making rayon (artificial silk), in oil refining and in the manufacture of explosives; but there is hardly any industry which at some stage or other does not make use of sulphuric acid.

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[1] It also gives us a means of estimating the amount of sulphate in a mixture (pp. 406–7).

Questions

N.B. *See note in italics*, p. 132

1. Sketch and label, *without* further description, the apparatus you would set up to prepare a small specimen of sulphur trioxide. Describe the appearance of this substance.

What takes place and what is formed when (*a*) the oxide is cautiously added to water; (*b*) the oxide is strongly heated; (*c*) concentrated sulphuric acid is heated with copper? *Oxf.*

2. Give the meaning of the term *catalyst* and illustrate with a reaction involving the use of a catalyst. *Dur.* (*part*)

3. Outline by the aid of a labelled diagram the contact process for the manufacture of sulphuric acid.

Explain what would be seen to happen when concentrated sulphuric acid is added to (*a*) a strong solution of cane sugar; (*b*) common salt; (*c*) potassium bromide crystals. *Lond.*

4. Give *one* method for the manufacture of sulphuric acid. Give *one* example to illustrate *each* of the following uses of sulphuric acid: (*a*) as a source of hydrogen; (*b*) as an oxidising agent; and (*c*) in the preparation of another acid. *Dur.*

5. Work out the equation which represents the burning of copper pyrites, $CuFeS_2$. (N.B. Remember that, on burning, all the elements form their respective oxides. Cf. the equation at the bottom of p. 303.)

6. If copper pyrites is used for the manufacture of sulphuric acid and there is no waste, what weight of sulphuric acid would be obtained per ton of pyrites burnt?

7. In what way is the chemical behaviour of sulphuric acid related to its high boiling-point?

8. Describe briefly *three* reactions which indicate the affinity of sulphuric acid for water, or for the elements of water. *Lond.* (*part*)

9. Give examples of the action of sulphuric acid (i) as an acid, (ii) as an oxidising agent. *O.C.* (*part*)

10. What broad differences can be recognised between the action on metals of (i) hot concentrated, (ii) cold concentrated, and (iii) dilute sulphuric acid. Give an example in each case.

11. What do you understand by an *acid* and an *acid salt*? Give *one* example of each.

How would you show by experiment that sulphuric acid has a basicity of at least 2? *Lond.* (*part*)

12. Explain what is meant by the *basicity* of an acid, and illustrate your answer by means of *three* acids of different basicity.

The molecular weight of an acid is known to be 92. 50 c.c. of a solution of this acid containing 30 gm. per litre were found to require for complete neutralisation 32·6 c.c. of a solution of caustic soda which contained 40 gm. per litre. Calculate the basicity of the acid. *Lond.*

13. 10 gm. of a specimen of sodium carbonate containing water of crystallisation require for complete neutralisation 3·43 gm. of sulphuric acid. Calculate the formula of the carbonate.

Lond. (*part*)

CHAPTER 27

SULPHIDES

The termination *-ide* in chemistry is worth noting—we have it in oxide, sulphide, chloride, etc. It usually indicates that the compound contains only two elements, oxygen (sulphur, chlorine, etc.) and one other. Thus lead oxide contains only lead and oxygen, copper sulphide contains only copper and sulphur, and so on.

Sulphides of metals occur very widely in nature, e.g. lead sulphide (galena), PbS; iron disulphide (iron pyrites), FeS_2; zinc sulphide (zinc blende), ZnS; mercuric sulphide (cinnabar), HgS, etc. In most cases these sulphides are used as sources of the metal.

Preparation. When we wished to prepare an *oxide* of an element we heated that element with oxygen. If we wish to prepare a *sulphide* we heat the element with sulphur. Probably you have at some time heated a mixture of iron filings and sulphur. The mass glows with an intense fiery red colour, and ferrous sulphide (FeS) is produced. Copper sulphide and a number of others may be prepared in a similar way.

Another important method of preparing sulphides will be considered presently (p. 310).

Properties. Generally speaking, *when a sulphide is heated in the air both its elements are converted into oxides.* We often have an example of this in the burning of an ordinary fire. Coal frequently contains small quantities of 'iron pyrites,' a sulphide of iron having the formula FeS_2. It is seen as thin golden layers when coal is being broken up. When burnt, the iron becomes ferric oxide (Fe_2O_3), and the sulphur becomes sulphur dioxide, according to the equation

$$[2FeS_2 + 11O = Fe_2O_3 + 4SO_2]$$
$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$$

It has been calculated that British chimneys every year send over two million tons of sulphur dioxide into the atmosphere—

a far greater amount than is used in our sulphuric acid manufacture.

In an ordinary way we do not notice the sulphur dioxide (gas with choking smell of burning sulphur) because it goes up the chimney, but it can be smelt when live coals are being carried on a shovel. The ferric oxide will be found among the ashes as reddish-brown fragments, easily crushed between the fingers.

Similarly when hydrogen sulphide is burnt, oxide of hydrogen (water) and sulphur dioxide are produced (p. 307).

When an acid is added to a sulphide the gas hydrogen sulphide is usually produced. We shall have an example of this presently.

Hydrogen Sulphide. It has already been mentioned that many sulphides can be made by heating together the two elements concerned. To make hydrogen sulphide (often called ***sulphuretted hydrogen***) by this method we place a quantity of sulphur in a wide test-tube (a 'boiling-tube'), fitted with a cork carrying two tubes, A and B, as shown in fig. 27/1. We heat the sulphur until it boils, and then connect the tube A to a hydrogen-generating apparatus. After a little while the gas coming from B begins to have a smell of bad eggs, and it blackens a bit of filter-paper that has been dipped in lead acetate solution. It is hydrogen sulphide

$$H_2 + S = H_2S$$

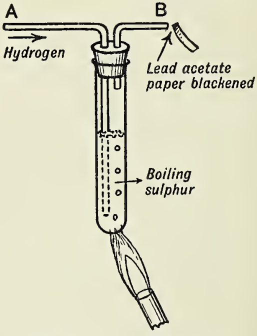

Fig. 27/1. Synthesis of hydrogen sulphide

The method just described is a very inconvenient one, and nobody ever uses it if a supply of hydrogen sulphide is required. It is important, however, for one reason—it shows that the gas we are considering really does contain hydrogen and sulphur, since it has been prepared from these elements.

Notice that we have here another example of a *synthesis*—the gas has been *synthesised* from its elements.

If we really want to prepare hydrogen sulphide starting from sulphur, much the best method is *first* to heat powdered sulphur with iron filings, so converting it into ferrous sulphide (p. 13). On adding dilute hydrochloric or sulphuric acid to this, the gas is readily evolved. In practice, we are usually provided with a supply of ferrous sulphide. The gas dissolves rather easily in cold water, but may be collected over hot water (fig. 27/2).

If we want the *dry* gas, we may dust the inside of a U-tube with phosphorus pentoxide, pass the gas through and collect it by displacing air upwards.[1] Phosphorus pentoxide (P_2O_5) is a rather unusual drying agent, but in the case of hydrogen sulphide none of the ordinary ones will serve. The gas is decomposed by sulphuric acid

$$H_2SO_4 + H_2S = 2H_2O + SO_2 + S$$

and is readily absorbed by quicklime and by sticks of caustic soda (forming calcium sulphide and sodium sulphide respectively). It is also decomposed by calcium chloride:—

$$CaCl_2 + H_2S = CaS + 2HCl$$

However, the last reaction takes place only very slowly, so fused calcium chloride is sometimes used for drying the gas, though it is not quite the ideal substance.

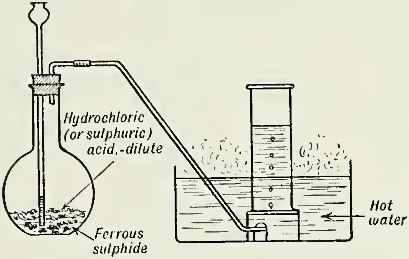

FIG. 27/2. Preparation of hydrogen sulphide

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[1] Not very satisfactory, because the gas is not *much* heavier than air. We could collect it over mercury (on which the dry gas acts only very slowly), but this is terribly expensive unless we work on a small scale (e.g. porcelain mortar as pneumatic trough, and test-tube as gas-jar).

The action of the dry gas upon mercury is so slow that for practical purposes it may be ignored.

Hydrogen sulphide is wanted so often in the laboratory that it has to be 'on tap,' and various pieces of apparatus have been devised to make this possible. The commonest one is 'Kipp's apparatus' shown in fig. 27/3. When the tap T is opened, the acid runs down the central stem and into the bottom bulb C, after which the level rises until the acid has flooded the ferrous sulphide in the middle bulb B. Gas now begins to be produced. On turning off the tap the pressure of gas in B increases, and pushes the acid back, up the central stem. When a supply of gas is required we have only to open T. The stored-up gas rushes out, and the cycle of events already described is repeated.

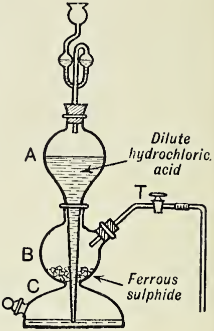

FIG. 27/3
Kipp's apparatus

The action is represented by the equation

$$\underset{\substack{\textit{Ferrous}\\ \textit{sulphide}}}{FeS} + 2HCl = \underset{\substack{\textit{Ferrous}\\ \textit{chloride}}}{FeCl_2} + \underset{\substack{\textit{Hydrogen}\\ \textit{sulphide}}}{H_2S}$$

The product always contains hydrogen, owing to the presence of free iron in the ferrous sulphide. However, if the gas is passed into a solution of antimony chloride, $SbCl_3$, an orange-coloured precipitate of antimony sulphide, Sb_2S_3, is produced. This may be filtered and washed, and then treated with hydrochloric acid, when pure hydrogen sulphide is obtained.

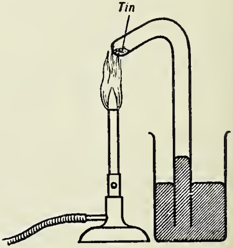

FIG. 27/4. Composition of hydrogen sulphide

Proof of Formula. When tin is heated in hydrogen sulphide it combines with the sulphur, and the hydrogen is set free. If the hydrogen sulphide is enclosed in a tube partly filled with mercury, as in fig. 27/4, it is found that the volume of the hydrogen left is equal to that of the original gas, i.e.:—

1 vol. of hydrogen sulphide contains 1 vol. of hydrogen (i).

Suppose 1 vol. of hydrogen sulphide contains n molecules.
∴ 1 vol. of hydrogen also contains n mols. (AVOGADRO).
∴ instead of (i) we may write
n mols. hydrogen sulphide contain n mols of hydrogen.
∴ 1 mol. ,, ,, ,, 1 mol. ,, ,,
But 1 molecule of hydrogen contains 2 atoms.
∴ 1 mol. of hydrogen sulphide contains 2 atoms of hydrogen, i.e. its formula is H_2S_x, where x remains to be found.
Now the density of hydrogen sulphide (calling that of hydrogen 1) is found by experiment to be 17.
∴ its molecular weight is 34 (p. 126).
We know that the hydrogen present in the molecule weighs 2 units (wt. of 2 atoms).
∴ wt. of sulphur $= 34 - 2 = 32$.
But 32 is the weight of 1 atom of sulphur.
∴ $x = 1$, and the formula is H_2S.

Properties. Hydrogen sulphide is colourless, and has a characteristic smell of bad eggs. It is slightly heavier than air. Its solubility has already been described.

A solution of hydrogen sulphide is slightly acid to litmus. As in the case of other acids, the hydrogen can be replaced by metals giving *salts*. Thus on replacing with sodium, H_2S gives us Na_2S, sodium sulphide. We may have only one of the hydrogen atoms replaced, in which case sodium hydrogen sulphide (or hydrosulphide), NaHS, is formed. If we replace with copper (divalent) we get CuS, copper sulphide, and so on. The sulphides, in fact, are to be regarded as salts.

Hydrogen sulphide burns readily with a blue flame, water and sulphur dioxide being produced

$$[H_2S + 3O = H_2O + SO_2]$$
$$2H_2S + 3O_2 = 2H_2O + 2SO_2 \quad \text{(i)}$$

One may easily detect the sulphur dioxide by putting one's nose about 6 in. above the flame. To detect the water we could make the flame play against the cooled surface of a retort, as in fig. 10/2. If this is done, a yellow deposit of *sulphur* will also be noticed on the retort. This is because, inside the flame, the hydrogen sulphide has been decomposed into its elements by the heat, and some of the sulphur is deposited on the cold surface. A similar result is obtained if we hold a candle flame against the retort, but in this case the element deposited is not sulphur but carbon.

When the supply of air is limited some of the sulphur escapes oxidation:—

$$[H_2S + O = H_2O + S] \quad . \quad . \quad . \quad (ii)a$$
$$2H_2S + O_2 = 2H_2O + 2S \quad . \quad . \quad . \quad (ii)$$

Hydrogen sulphide is present among the gases emitted from volcanoes, and some of the sulphur found in such districts may have been formed by this reaction. Another possible explanation is given on p. 284.

Since both the elements present in hydrogen sulphide combine readily with oxygen, we should expect to find that it is a reducing agent. This is actually the case. In fact, nearly all the properties of hydrogen sulphide fall into two groups.

(A) It is a reducing agent.

(B) It readily undergoes double decomposition with solutions of salts, causing other sulphides (and acids) to be produced.

We will deal with its remaining properties under these two heads.

(A) *Hydrogen Sulphide a Reducing Agent.* Before studying this section you had better read again the paragraph on 'Reduction and Reducing Agents' (pp. 278–280).

We have already had examples of the fact that hydrogen sulphide is a reducing agent. It reduces sulphuric acid to sulphur dioxide (p. 305), sulphur dioxide to sulphur (p. 284) and chlorine to hydrogen chloride (p. 253; $Cl_2 + H_2S = 2HCl + S$). The reaction with chlorine suggests that similar ones would probably take place with bromine and iodine, and this is actually the case (you can write the equations for yourself). On these reactions is based a method which is sometimes used for the preparation of hydrobromic or hydriodic acid. Hydrogen sulphide is bubbled through bromine that has been covered with a quantity of water. When the reddish colour of the water has disappeared, the liquid is filtered to get rid of the sulphur,[1] and a solution of hydrobromic acid remains. A similar method is used for hydriodic acid.

Another example of the reducing action of hydrogen sulphide is seen in the fact that a solution of ferric chloride (yellow) is converted into one of ferrous chloride (green), sulphur being also produced.[2]

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S$$

(In constructing this equation, note first that $FeCl_3$ has to become $FeCl_2$, i.e. it must lose *one* atom of chlorine. But the H_2 (in H_2S) will evidently combine with *two* atoms. To provide the two atoms of chlorine we must start with $2FeCl_3$.)

Before leaving this part of the subject, it is worth noting that when hydrogen sulphide undergoes oxidation, it is usually the *hydrogen* which is oxidised, the sulphur being set free. An obvious exception is that when the gas burns, both elements are oxidised. Even in this case, if the supply of air is insufficient, it is the sulphur which escapes oxidation. The equations have already been given.

(B) *Double Decomposition with Salts.* As already mentioned (p. 153), a double decomposition may be defined as a reaction of the type

$$AX + BY = AY + BX$$

For instance, if hydrogen sulphide is passed through a solution of copper sulphate, we have

$$CuSO_4 + H_2S = CuS + H_2SO_4$$

(A being represented by Cu, X by SO_4, B by H_2, and Y by S). Copper sulphide is precipitated (i.e. formed as an insoluble substance which gradually settles to the bottom).

With lead nitrate solution, a very similar action takes place:—

$$\underset{\textit{Lead nitrate}}{Pb(NO_3)_2} + H_2S = \underset{\textit{Lead sulphide}}{PbS} + \underset{\textit{Nitric acid}}{2HNO_3}$$

---

[1] Precipitated sulphur is very finely divided, so a close-textured filter-paper is needed.

[2] Do not make the mistake—a very common one—of saying that when the gas is passed through a solution of ferric chloride, ferric sulphide is precipitated.

In either case, on filtering, the sulphide remains on the paper. The *filtrate* (i.e. the liquid which comes through) is boiled for a minute or two to get rid of the excess of gas. We are then left with a dilute solution of sulphuric or nitric acid, as the case may be.

Notice that we have here a means of preparing any sulphide that happens to be insoluble—and most sulphides are. We take a soluble salt of the metal in question and pass hydrogen sulphide through its solution. At the same time the acid corresponding to the soluble salt is also obtained. The method is, in fact, a fairly general one for preparing both sulphides and acids.

On passing hydrogen sulphide through a solution of sodium hydroxide, $NaOH$, we do *not* obtain a precipitate of sodium sulphide (or rather sodium hydrosulphide, $NaHS$), because this substance is soluble in water. It is obtained, however, on evaporating to dryness.

$$NaOH + H_2S = NaHS + H_2O$$

We can now understand why hydrogen sulphide is so much used in analysis. Suppose we have a mixture of copper sulphate, zinc nitrate and sodium chloride, and we wish to separate the three metals, or rather compounds containing the metals.

We make a solution in water, acidify with hydrochloric acid and pass hydrogen sulphide. Copper sulphide only is precipitated, because copper is the only one of the three metals whose sulphide is *insoluble in acid.*

We filter off the copper sulphide, boil the filtrate to expel excess of hydrogen sulphide and make it alkaline by adding ammonia. On passing hydrogen sulphide once more, zinc sulphide is precipitated, because though soluble in acid, it is *insoluble in a neutral or alkaline solution.*

We filter again. The filtrate will contain sodium hydrosulphide, because this is *soluble both in acid and in water.*

Thus by means of hydrogen sulphide we can separate metals into three groups: (i) those such as copper, whose sulphides are insoluble in hydrochloric acid; (ii) those like zinc, whose sulphides are soluble in hydrochloric acid but are insoluble in water; and (iii) those such as sodium, whose sulphides are soluble in water.

We will conclude this chapter by noticing a few cases in which sulphides are formed in common experience.

In many manufacturing towns silver articles tarnish very rapidly. This is because the silver on the surface is turned into silver sulphide by traces of hydrogen sulphide in the atmosphere. Oil-paintings go very dark for the same reason. 'White lead' (lead carbonate) is a very common ingredient of paint, and this is gradually turned into black lead sulphide. You may have noticed that a sixpence goes very dark if kept in the same pocket with a piece of india-rubber. Remembering how rubber is vulcanised (p. 275), you will, no doubt, be able to explain what has happened. A silver spoon tarnishes if it is used with egg or mustard, both of which contain compounds of sulphur.

Questions

N.B. *See note in italics*, p. 132

1. Describe, with a diagram, how you would prepare and collect several jars of hydrogen sulphide. What reactions take place between this gas and (*a*) ferric chloride solution, (*b*) sodium hydroxide solution.

If 112 c.c. of hydrogen sulphide is mixed with 120 c.c. of chlorine at N.T.P., what weight of sulphur is formed? *Camb.*

2. Draw a labelled diagram of a Kipp's apparatus suitably charged to provide a supply of hydrogen sulphide whenever it may be required.

3. You are provided with iron filings, powdered sulphur, concentrated hydrochloric acid, water and the usual laboratory apparatus, including a lighted bunsen burner, but no other chemicals. Explain carefully how you would prepare and collect some reasonably pure hydrogen sulphide.

What is the reaction of this gas with solutions of (*a*) lead nitrate (or lead acetate), (*b*) litmus, (*c*) ammonia, (*d*) ferric chloride? *J.M.B.*

4. Give a short account of an experiment by which it may be shown that hydrogen sulphide contains its own volume of hydrogen. Assuming that the density of the gas relative to hydrogen is 17, and that the atomic weight of sulphur is 32, show how to arrive at the formula H_2S.

5. Describe and explain what happens when hydrogen sulphide is passed (*a*) into bromine water; (*b*) into a solution of sulphur dioxide, (*c*) over paper moistened with lead acetate solution. *Lond.* (*part*)

6. Show how by means of hydrogen sulphide we are able to divide metals into three groups.

7. Why is it important that coal-gas should be free from hydrogen sulphide? How could you find out whether a given sample of coal gas was pure in this respect?

8. Describe the preparation and collection of hydrogen sulphide.

Describe an experiment by which you would show that this gas is a reducing agent, explaining clearly the reduction that has taken place.

Name three methods of salt formation which could be applied to the making of sulphides, and give an example of the preparation of a sulphide by each method. *Scot. L.C.* (*part*)

9. What volume of hydrogen sulphide, measured at 12° C. and 75·6 cm. pressure, would be required to precipitate all the copper from a solution containing 2·5 gm. of crystallised copper sulphate, $CuSO_4{\cdot}5H_2O$?

10. What volume of hydrogen sulphide would be just sufficient to precipitate all the sulphur from 84·6 c.c. of sulphur dioxide, all measurements being made at room temperature and pressure?

11. Account for the following facts:
- (i) When standing near a shovelful of burning coals taken from a fire, one can smell sulphur dioxide.
- (ii) Silver articles exposed to the air of towns quickly tarnish.
- (iii) A silver coin kept in a pocket with a piece of india-rubber soon tarnishes, and so does a silver spoon that has been used in egg or mustard.
- (iv) Oil-paintings go very dark with age.

CHAPTER 28

AMMONIA

AMMONIA is found is Nature, being produced during the decay of organic matter, and especially of some of the matter present in the excreta of animals; so that it can often be smelt near a decaying manure heap or in a badly ventilated stable. Very large quantities are now being manufactured by the synthetic process described on p. 322, and a considerable amount is also obtained from crude goal-gas by bringing the latter into contact with water, ammonia being extremely soluble. A strong solution of ammonia may be used to obtain a quantity of the gas for examination. The apparatus is as shown in fig. 28/1, except that instead of the wide test-tube we use a flask fitted with a thistle funnel.

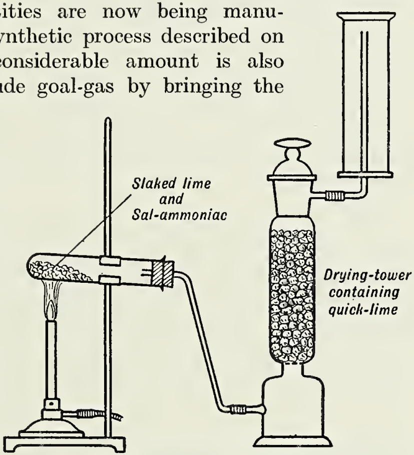

FIG. 28/1. Preparation of dry ammonia

In answering a question on the preparation of ammonia, you would be expected to describe the method illustrated in fig. 28/1, where the wide test-tube[1] contains a mixture of slaked lime and ammonium chloride (the equation is given on p. 319). This is not so convenient as using a solution of ammonia, but it may fairly be objected that in the latter case we are not really 'preparing' the gas—it has already (in solution) been prepared for us.

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[1] For the slight downward slope, see p. 25 (footnote). A test-tube is used instead of a flask so that, if breakage should occur, the loss may not be so serious.

If the gas is required *dry*, we must pass it through a tower containing quicklime. We cannot use calcium chloride because ammonia combines with this substance. It also combines with sulphuric acid, as we shall see in the course of the present chapter.

Ammonia is not much more than half as heavy as air. It is therefore collected by displacing air downwards as shown. It may also be collected over mercury.

The earlier chemists found it difficult to isolate these very soluble gases. It was Priestley, in 1774, who thought of collecting them over *mercury*. He had succeeded in obtaining hydrogen chloride by heating hydrochloric acid and collecting the gas over mercury as already mentioned. With similar apparatus he now tried the effect of heating 'volatile spirit of sal-ammoniac' (i.e. a solution of ammonia) and obtained ammonia.

It is found to be a colourless gas with a very characteristic smell. We have already spoken of its lightness and its great solubility. At 0° C. 1 volume of water will dissolve over 1100 volumes of ammonia. On account of its great solubility it lends itself well to the 'fountain experiment' described on p. 241.

When passing ammonia gas into water to prepare a solution, it is advisable to adopt some such arrangement as that shown in fig. 23/3 (p. 266); otherwise the liquid is very likely to be 'sucked back.'

When ammonia is passed into water the weight of the liquid, of course, increases, but there is a more than proportionate increase in the volume. The result is that as the solution becomes stronger its *density* becomes less. A saturated solution of ammonia, at 15°, has a relative density of 0·88. The gas is comparatively easy to liquefy.

We now come to its chemical properties.

A lighted taper plunged into the gas is promptly extinguished.

If ammonia (dried by being passed through a tower of quicklime) is passed over heated copper oxide, some interesting changes take place. A suitable form of apparatus is shown in fig. 28/2. Water collects in the U-tube and nitrogen in the bottle. (The water, as we should expect, contains dissolved ammonia.) The copper oxide is reduced to copper.

Now the water formed is a compound of hydrogen and oxygen, and only the oxygen could have been obtained from the copper oxide. The hydrogen must have come from the ammonia, and so must the nitrogen. Clearly ammonia contains nitrogen and hydrogen. We shall see presently that ammonia is made on a large scale by using nitrogen and hydrogen *only*, a proof that no other elements are present. Its formula is actually NH_3. Its action on copper oxide may be expressed by the equation

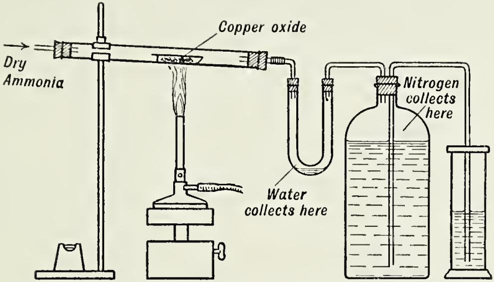


FIG. 28/2. Ammonia contains nitrogen and hydrogen

$$3CuO + 2NH_3 = 3H_2O + 3Cu + N_2$$

It is difficult to answer the question 'Does ammonia burn?' with a plain 'Yes' or 'No.' If in fig. 28/1 we suppose the gas-jar to be removed and a lighted taper to be held to the mouth of the upturned tube, the ammonia burns with a brownish flame *so long as the taper is held in position.* As soon as the taper is withdrawn, the ammonia ceases to burn. The fact is that the heat of the taper decomposes the gas into its elements, and it is the hydrogen which burns, nitrogen escaping unchanged into the air:—

$$[2NH_3 + 3O = 3H_2O + N_2]$$
$$4NH_3 + 3O_2 = 6H_2O + 2N_2$$

Ammonia will burn if surrounded with oxygen. The method of carrying out the experiment will be sufficiently clear from fig. 28/3. The cotton-wool serves to distribute the supply of oxygen more evenly round the central tube.

In connection with the manufacture of sulphuric acid, we saw that ammonia can be oxidised to *nitric oxide* if platinum gauze is present to act as a catalyst (for equation, etc., see p. 352). The reaction may be illustrated in the laboratory by the apparatus of fig. 28/4. A *slow* current of oxygen is passed through strong ammonia contained in a conical flask. A spiral of thin platinum wire is then heated to redness and plunged into the upper part of the flask. Brown fumes are produced because the nitric oxide first formed is afterwards oxidised to nitrogen peroxide; and the heat of the reaction causes the platinum to continue glowing.

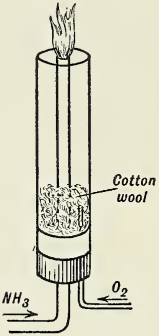


FIG. 28/3. Ammonia burning in oxygen

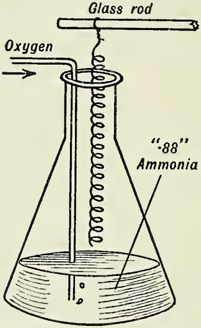


FIG. 28/4. Catalytic oxidation of ammonia

As usually obtained, ammonia readily turns red litmus paper blue. (A good test, for no other common gas does this.) Carefully dried ammonia, however, has no effect on litmus. A solution in water at once turns it blue. It is fair to suppose that some chemical change takes place when ammonia dissolves in water. This change may be expressed by the equation

$$NH_3 + H_2O \quad = \quad \underset{\textit{Ammonium hydroxide}}{NH_4OH}$$

As a matter of fact, only a *little* of the ammonia undergoes this chemical change, most of the gas being simply dissolved, just as oxygen might be dissolved.

On boiling a solution of ammonia, the ammonium hydroxide is decomposed ($NH_4OH = NH_3 + H_2O$), and the whole of the ammonia is expelled, pure water being left.

It is important to notice the resemblance between the formulæ NH_4OH, $NaOH$, $Ca(OH)_2$, etc. We have already seen (p. 45) that the $-OH$ group has a valency of one, so that the atom of sodium (univalent) combines with *one* such group, forming sodium hydroxide, $NaOH$, while the atom of calcium (divalent) combines with *two*, forming calcium hydroxide, $Ca(OH)_2$. The group NH_4 resembles the atom of sodium. It is univalent, combining with a single OH group.

Now the hydroxides of sodium, calcium and other metals are *basic*, i.e. they react with acids forming a salt and water only, e.g.

$$NaOH + HCl = NaCl + H_2O$$

$$Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O$$

Ammonium hydroxide behaves in a similar way:—

$$NH_4OH + HCl = NH_4Cl + H_2O$$

We begin to see that 'ammonium' forms a whole series of compounds quite similar to those formed by sodium.

We may compare

ammonium hydroxide NH_4OH	with	sodium hydroxide $NaOH$
ammonium chloride NH_4Cl	,,	sodium chloride $NaCl$
ammonium nitrate NH_4NO_3	,,	sodium nitrate $NaNO_3$
ammonium sulphate $(NH_4)_2SO_4$	,,	sodium sulphate Na_2SO_4

and so on.

Do not confuse *ammonia* and *ammonium*. Ammonia is the gas, NH_3; ammonium is a group ('radical' is the correct term) having the formula NH_4. It is found only in compounds. Many attempts have been made to isolate it, but so far without success. The termination *-um* was given to it because its compounds (salts, etc.) resemble the compounds of metals, *-um* being the recognised termination in chemistry for a metal.

We have already seen that the salt ammonium chloride can be produced by neutralising ammonium hydroxide with hydrochloric acid. It can also be produced, however, by bringing the two gases together. If you dip a glass rod into hydrochloric acid, and bring it near the mouth of a test-tube from which ammonia is being evolved, you will see dense white fumes which consist of ammonium chloride:—

$$NH_3 + HCl = NH_4Cl$$

The production of these fumes is sometimes used as a rough test for ammonia. The litmus test just mentioned is a much better one, but the smell of ammonia is so characteristic that it is not often necessary to fall back on other tests.

It is worth noticing that the gas ammonia is not, strictly speaking, a *base*, because a base reacts with an acid to produce a salt *and water* only. Ammonia gives us the salt (e.g. ammonium chloride in the case just discussed), but no water. Ammonium hydroxide would give us both ($NH_4OH + HCl = NH_4Cl + H_2O$), and is therefore a true base.

Since ammonia only lacks the elements of water in order to make it into a true base, it is sometimes called the *anhydride of a base*.

In the gas-works the solution of ammonia obtained is usually neutralised with *sulphuric* acid:—

$$2NH_4OH + H_2SO_4 = (NH_4)_2SO_4 + 2H_2O$$

If we wished to make ammonium nitrate we should neutralise the solution with *nitric* acid:—

$$NH_4OH + HNO_3 = NH_4NO_3 + H_2O$$

We have seen how to obtain an ammonium salt from ammonia. It is important to be able to carry out the reverse process, i.e. to obtain ammonia from an ammonium salt. This is very readily done by heating the salt with a base such as sodium hydroxide or calcium hydroxide, e.g.

$$NH_4Cl + NaOH = NaCl + NH_3 + H_2O$$
$$(NH_4)_2SO_4 + Ca(OH)_2 = CaSO_4 + 2NH_3 + 2H_2O$$

etc.

This reaction also is made use of in the gas-works, for on passing the crude coal-gas through water the latter is found to have extracted not only ammonia, but also *ammonium salts*. Before adding sulphuric acid it is necessary to make these salts give up their free ammonia, and this is done by boiling the solution with milk of lime, $Ca(OH)_2$. Steam is then blown through the solution, and this has the effect of expelling the ammonia, which is at once passed into the sulphuric acid. We have already seen that this reaction between calcium hydroxide and an ammonium salt (usually the chloride) is used for preparing the gas in the laboratory. The equation is

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2H_2O + 2NH_3$$

This evolution of ammonia gives us a very convenient test for an ammonium salt. We have only to warm the substance in a test-tube with a little slaked lime and see if the gas is evolved.

For convenience a solution of caustic soda (properly 'sodium hydroxide,' NaOH) is generally used instead of slaked lime. Write the equation for yourself—it is easier than the one just given.

In the laboratory, ammonium hydroxide is often used to form the hydroxides of certain metals. Suppose, for instance, that it is added to a solution of ferric chloride ($FeCl_3$). A brown precipitate of ferric hydroxide is at once produced:—

$$FeCl_3 + 3NH_4OH = Fe(OH)_3 + 3NH_4Cl$$

The precipitate could be separated by filtration, and in this way iron could be completely removed from the solution. Thus we can separate metals which form insoluble hydroxides from those which do not, a process which is often very useful in the course of analysis. You may remember that hydrogen sulphide is used in a somewhat similar way for separating metals which form insoluble *sulphides* from those which do not.

With copper sulphate, ammonia gives a solution of a beautiful deep-blue colour. This is due to the formation of *cuprammonium hydroxide*, a substance of rather complex composition. The solution possesses the curious property of dissolving cellulose (cotton-wool, filter-paper, etc.).

We might notice that though ammonium hydroxide and sodium hydroxide are very similar in their chemical behaviour, they differ in their reactions with copper sulphate. Ammonium hydroxide, as just mentioned, gives a deep-blue *solution*, while sodium hydroxide gives a pale-blue *precipitate* (of copper hydroxide, $Cu(OH)_2$).

The reaction between ammonia and chlorine has already been considered in connection with chlorine (p. 253). This reaction is occasionally used as a means of preparing *nitrogen*. Chlorine is first washed (to remove hydrogen chloride) by passing it through a little water in a Woulff bottle, and the gas then passes through two more Woulff bottles, each containing strong ammonia. The liberated nitrogen is then collected over water in the usual way. The apparatus is as shown in fig. 17/3, except that there would be three bottles instead of two.

It is very important that the ammonia should be in *excess*, because otherwise the dangerously explosive compound nitrogen trichloride, NCl_3, may be formed. Dulong was examining this compound in 1811, when it exploded, with the result that he lost two fingers and one eye. As soon as he was convalescent he continued his examination of nitrogen trichloride! It was the same Dulong who eight years later, working with Petit, established the law connecting specific heat with atomic weight (p. 66).

Proof that Formula is NH_3. The production of nitrogen by the action of chlorine on ammonia can be used to play an important part in establishing the formula NH_3. (It does not actually give us the formula.) The method was devised by A. W. Hoffmann.

A long tube AB, divided by rubber bands into three equal parts, is filled with chlorine. The tube is fitted with a rubber stopper through which there passes a dropping funnel filled with strong ammonia solution. The tap of the funnel is cautiously turned to admit a drop of the liquid. There is a flash of light, and thick fumes are produced. More solution is admitted, drop by drop, until there is no further action.

The solution remaining in the funnel is now emptied, and replaced by dilute sulphuric acid. Some of this is allowed to run into the tube to remove the excess of ammonia. (The funnel must not be allowed to become empty, or air will be drawn into the tube and the experiment will be spoilt.)

The funnel is now filled with water, and a rubber stopper carrying the tube CDE is inserted. CDE has previously been filled with water by suction, the water being prevented from running out again by closing the clip at D.

On opening the clip and the tap of the funnel, water is drawn into the tube. The beaker is raised or lowered until the water in it and in the tube are at the same level. The gas in the tube is therefore at atmospheric pressure, and it is found to occupy one-third of the tube, and to consist of nitrogen. We must now see what we can conclude from these results.

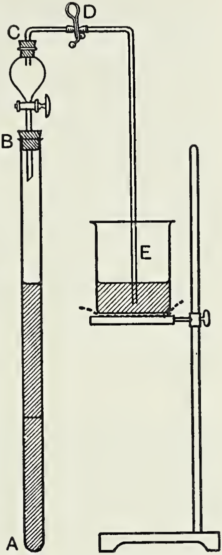


Fig. 28/5. Composition of ammonia

We assume (p. 243) that chlorine combines with an equal volume of hydrogen. Therefore the original 3 volumes of chlorine would combine with 3 volumes of hydrogen. The *nitrogen* with which this hydrogen was originally combined remains in the tube, and evidently occupies *one* volume.

Thus ammonia consists of 1 volume of nitrogen combined with 3 volumes of hydrogen. (i)

Suppose 1 volume of nitrogen contains x molecules.

∴ 1 volume of hydrogen contains x molecules (Avogadro)

∴ 3 volumes ,, ,, $3x$,,

Instead of (i) we may therefore write

> ammonia consists of x molecules of nitrogen combined with $3x$ molecules of hydrogen, or (cancelling by x) of 1 molecule of nitrogen combined with 3 molecules of hydrogen.

Assuming that the molecules of nitrogen and hydrogen both contain 2 atoms, we see that ammonia contains nitrogen and hydrogen in the proportion of 2 atoms to 6 atoms, or 1 atom to 3 atoms. *This is as far as we can get from this experiment*—the formula is either NH_3, or N_2H_6 or N_3H_9, etc.

To decide between these possible formulæ, we find the density of ammonia relative to hydrogen. This is found to be 8·5, so that the molecular weight is $2 \times 8{\cdot}5 = 17$. Therefore the formula must be NH_3 (N_2H_6, for instance, would give a molecular weight of 34).

Synthetic Ammonia. On the small scale, as we have seen, ammonia is prepared by heating an ammonium salt (usually the chloride) with slaked lime. On the large scale it is synthesised from its elements, nitrogen and hydrogen, and because of the way it is made, the product is often called 'synthetic ammonia,' though it is, of course, just the same as ammonia prepared by any other method.

The reaction concerned appears at first sight to be a very simple one—merely the combination of nitrogen with hydrogen,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

The arrow marks remind us that we are dealing with a *reversible* reaction. The fact is that nitrogen and hydrogen combine only under special conditions, and the ammonia so produced shows a very strong tendency to decompose into its elements! First of all, then, we will consider the conditions that could lead to a successful manufacturing operation.

It would be a good plan at this stage to re-read what was said about reversible reactions on pp. 97–100. There, we were considering the action of steam on iron.

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$

By using a strong, sealed container we make it impossible for the hydrogen to escape, with the result that the *reverse* action sets in

$$Fe_3O_4 + 4H_2 = 3Fe + 4H_2O$$

We saw that in such circumstances (no possibility of escape for any of the reacting substances), the final result is that a *condition of equilibrium* is set up, in which all four substances are present in certain fixed proportions.

In the reaction we are now considering ($N_2 + 3H_2 \rightleftharpoons 2NH_3$), we shall once again be concerned with a state of equilibrium, and the chemist aims at two things

(1) that the equilibrium mixture (of nitrogen, hydrogen and ammonia) shall contain as high a percentage of ammonia as possible, and
(2) that the state of equilibrium shall be attained *quickly.*

To begin with (1). In the steam–iron case we saw that a condition of equilibrium can be altered by altering the conditions, e.g. by raising the temperature. If we do this, there is a period of readjustment, after which a *new* condition of equilibrium is set up—new, because the percentages of the various reacting substances will have a new constant value differing from that which obtained before the disturbance.

The same principle applies to the 'ammonia' reaction. Now, one condition which can easily be altered is that of pressure. Suppose, then, we have an equilibrium mixture of nitrogen, hydrogen and ammonia, what will be the effect of increasing the pressure?

In what follows, this would be an example of what is called 'applying a stress,' and the result is predicted in a Rule (or Law, or Principle) known as ***Le Chatelier's Rule.*** This states that, *If to a system in equilibrium a stress be applied, the equilibrium will be altered in such a direction as will tend to reverse the effect of the stress.*

At first sight, this general statement will seem very difficult to grasp. We shall begin to understand it better if we go back to our question—what will be the effect of increasing the pressure? When equilibrium is re-established, will the mixture contain a greater percentage of ammonia than before, or a less?

Applying Avogadro's Hypothesis we may write,

$$\begin{array}{ccccc} N_2 & + & 3H_2 & \rightleftharpoons & 2NH_3 \\ \text{1 vol.} & & \text{3 vols.} & & \text{2 vols.} \end{array}$$

i.e. *four* volumes of the nitrogen–hydrogen mixture give only *two* volumes of ammonia. If the three gases are in a confined space, we should, of course, have a reduction of pressure instead of a reduction of volume. According to Le Chatelier's Rule, then, the greater the pressure, the greater will be the percentage of ammonia in the equilibrium mixture, because the formation of ammonia is accompanied by reduction of pressure, which 'tends to reverse the effect of the stress.'

So the chemist decides to apply the highest possible pressure.[1]

Next, what will be the effect of raising the temperature of the equilibrium mixture?

The reaction $N_2 + 3H_2 = 2NH_3$ is *exothermic*, i.e. heat is given out as the gases combine (and correspondingly, heat is absorbed when ammonia decomposes). By Le Chatelier's Rule, then, if we 'apply a stress' by *raising* the temperature, more ammonia will be decomposed, since that reaction absorbs heat and so *reduces* the temperature. But 'ammonia decomposed' is just the opposite to what we want, so instead of a high temperature we think of working at a low one.[2] Why not at 15° C., say, since this is about average room temperature, and we should need to apply neither heat nor a refrigerant?

At this temperature, and under 300 atmospheres pressure, the equilibrium mixture would contain about 90 per cent. of ammonia. That seems excellent, *but*—

Chemical reactions are *slowed down* by reduction of temperature. This applies both to the 'forward' action $N_2 + 3H_2 = 2NH_3$, and to the 'reverse' action, $2NH_3 = N_2 + 3H_2$. Because of this slowing down, it takes a longer time to establish equilibrium. Under the conditions mentioned (300 atm., 15° C.) it would take months!

That, of course, is just hopelessly slow. At a higher temperature, equilibrium is established more quickly, but the product contains a lower percentage of ammonia. We cannot have it both ways.

At this point, the chemist will certainly look round for a suitable catalyst (p. 145). This will speed up both the direct action and the reverse one, and so equilibrium will be established more quickly, but without the reduction of yield that would have resulted from employing a very high temperature. Even with a catalyst, however, there is 'nothing doing' at so low a temperature as 15° C.

Summing up our results, then, we see that the conditions for successful manufacture will be

(i) the highest possible pressure (limited only by engineering difficulties),
(ii) a sort of 'compromise' temperature,
(iii) a suitable catalyst.

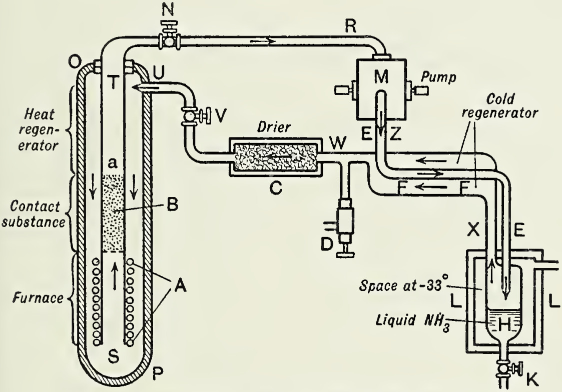
---

[1] It is convenient at this point to consider the same question in relation to the *iron oxide + hydrogen* reaction. Here there is *no change* of volume as the reaction proceeds (4 vols. hydrogen→4 vols. steam). Hence the proportions of hydrogen and steam in the equilibrium mixture are unaffected by change of pressure.

[2] In the steam–iron case the reaction $4H_2 + Fe_3O_4 = 4H_2O + 3Fe$ is *en*dothermic. Hence by raising the temperature, we shall get a higher percentage of steam and a lower percentage of hydrogen in the equilibrium mixture.

The manufacturing process we shall now describe is known as the Haber–Bosch process after its inventors. It was Bosch who showed how to obtain the necessary nitrogen–hydrogen mixture from air and water. First a mixture of producer-gas ($CO + N_2$) and water-gas ($CO + H_2$) is made by passing air and steam alternately over hot coke (p. 185). The complete mixture evidently contains nitrogen and hydrogen (which are needed), together with carbon monoxide (which is not). By passing the mixture together with steam over a catalyst (oxide of iron) we have the reaction $CO + H_2O = CO_2 + H_2$. The carbon dioxide is dissolved out by water under pressure,[1] and we now have just the nitrogen–hydrogen mixture we need, except that a little water vapour and carbon monoxide are still present as impurities. The monoxide is removed (at high pressure) by absorption in a solution of ammoniacal copper salts, while the water vapour is simply frozen out by strong cooling.

Having obtained the necessary mixture, let us see how it is converted into ammonia. First it is compressed to about 300–350 atmospheres by the pump M. It passes through the tube EE to the vessel H, and from there through the tube FF and the drier C (filled with soda-lime). At U it enters the



By arrangement with Sampson Low, Marston & Co Ltd

FIG. 28/6. Synthetic ammonia by the Haber process strong tube OP, where it is at first electrically heated so as to be at a temperature of about 500° C. when it passes over the contact substance, or catalyst, at B. After a little while the electric current can be switched off, the heat of reaction being sufficient to maintain the temperature at 500°.

---

[1] Solution used as a source of solid carbon dioxide (p. 174).

The catalyst consists of a very pure, spongy iron mixed with a small quantity of 'promoters' (usually a mixture of aluminium oxide, Al_2O_3, and potassium oxide, K_2O). In contact with it about 17 per cent. of the nitrogen and hydrogen combine to form ammonia. The 'equilibrium amount' would be about 23 per cent., but in practice the gases are not in the tube quite long enough for equilibrium to be established.

The mixture of ammonia with unchanged gases passes through M (where fresh supplies of nitrogen and hydrogen are pumped in) into the vessel H, which is kept at a temperature of about $-33°$ C. by surrounding it with ammonia previously liquefied (surrounding liquid not shown in diagram). At this temperature the gaseous ammonia liquefies, but the unchanged nitrogen and hydrogen pass on to go through the round of changes once more. Once these gases have been pumped into the apparatus they never leave it except as ammonia.

The 'heat exchange' arrangements are worth a passing notice. As the hot gases cool in their passage through the tube ST, they give up their heat to the cold gases passing downwards from U, with the result (already mentioned) that the latter no longer need to be electrically heated. Similarly, a glance at the figure will show that the gases entering H are strongly cooled by those which have just left it, while the leaving gases are *raised* in temperature before passing through the drier.

At higher pressures the proportion of nitrogen and hydrogen which combines is greater. In some works pressures up to 1000 atmospheres are employed, and 40 per cent. of the gases can then be made to combine in a single cycle.

The ammonia thus produced is for the most part turned into ammonium sulphate, $(NH_4)_2SO_4$. The SO_4 group may, of course, be obtained from sulphuric acid, but a much cheaper process is now in use, in which 'anhydrite' or native calcium sulphate, $CaSO_4$, is employed. This substance is suspended in water in which ammonia has been dissolved, and the suspension is then treated with carbon dioxide. Calcium carbonate is precipitated, and ammonium sulphate is readily obtained from the solution.

$$CaSO_4 + H_2O + 2NH_3 + CO_2 = CaCO_3 + (NH_4)_2SO_4$$

Important Ammonium Salts. *Ammonium sulphate,* $(NH_4)_2SO_4$, is largely used as a fertilizer.

Ammonium chloride, NH_4Cl, like many other ammonium salts, *volatilises* when heated, turning directly from solid to vapour. The vapour readily condenses as a *sublimate* on the cool sides of the test-tube, etc., in which the salt has been heated.

It can be shown that the change is not quite so simple as this, but that near the source of heat ammonia and hydrogen chloride are formed ($NH_4Cl = NH_3 + HCl$), and that these recombine in the cooler parts. The ammonium chloride in fact has been *dissociated* (p. 296). The dissociation is easily shown by heating a little ammonium chloride in a sloping tube with litmus papers placed as in fig. 28/7. The upper piece of litmus turns blue (ammonia), the lower one red (hydrogen chloride). The ammonium chloride has evidently been decomposed into ammonia and hydrogen chloride, and the lighter ammonia has for the most part [1] moved up the tube, while the heavier hydrogen chloride has moved down.

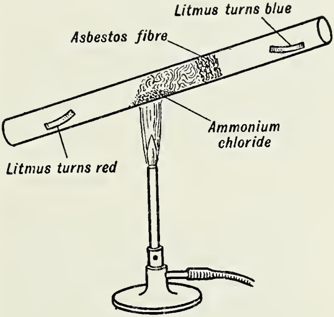


FIG. 28/7
Dissociation of ammonium chloride

Ammonium chloride is used in soldering, for cleaning the soldering iron (so called, no doubt, because the 'business end' of it is made of *copper*). When this is heated and dipped into solid ammonium chloride, the latter is dissociated just round the hot metal, and the hydrogen chloride, being a strongly acid gas, cleans the copper and enables the solder to stick to it.

---

[1] The separation is, of course, not complete. Owing to diffusion (Chapter 12) some of the lighter gas moves downwards, and vice versa.

Ammonium chloride is largely used in Leclanché cells and dry batteries.

Ammonium nitrate, NH_4NO_3, is used in preparing the 'laughing gas' employed by the dentist, for on heating, it breaks up according to the equation $NH_4NO_3=2H_2O+N_2O$ (nitrous oxide). Though not very explosive itself, it is often used as a constituent of explosive mixtures. Owing to the fact that it contains nitrogen both in the NH_4 group and in the NO_3 group, it is a very concentrated nitrogen fertilizer (but see p. 377).

Ammonium carbonate, $(NH_4)_2CO_3$, is an important constituent of smelling-salts and of certain baking powders.

Uses of Ammonia. Ammonia is used in ice-making and in connection with cold-storage, etc. The gas is contained in a system of 2-inch pipes, and by means of a pump and suitably arranged valves, high pressure is maintained on one side of the system (the right in fig. 28/8) and low pressure on the other. The gas is compressed into the coil surrounded by the condenser. Compression tends to make it hot (cf. the action of a bicycle pump), but the surrounding water prevents much rise of temperature, and as the gas is under high pressure it

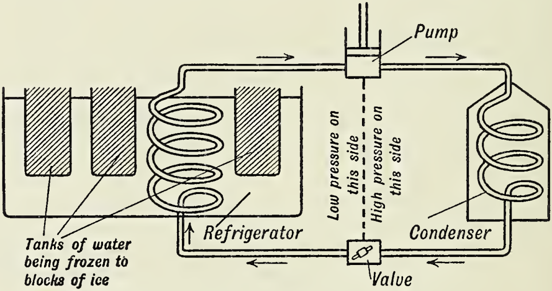

Pump
Low pressure on this side
High pressure on this side
Tanks of water being frozen to blocks of ice
Refrigerator
Condenser
Valve

FIG. 28/8. Ammonia used for ice-making

liquefies. This liquid ammonia flows to the low-pressure side at a speed which can be controlled by a regulating valve. On entering the low-pressure region the liquid rapidly vaporises and the necessary latent heat is absorbed through the coils from the surrounding liquid (usually brine), which is thus cooled considerably below 0° C. The cold brine may either be used to make ice, as indicated in the figure, or it may be made to flow through pipes arranged in cold-storage chambers. The ammonia, of course, cannot escape, and is alternately liquefied and vaporised again and again. Note that the ammonia must be free from water—we are dealing with *liquid* ammonia, not with ammonia solution.

As a refrigerant, however, ammonia is being gradually replaced by the gas *freon*, CF_2Cl_2, which besides possessing the essential property of being easily liquefied, is odourless, non-inflammable, non-poisonous and without corrosive action on most ordinary metals.

Ammonia is also used as a source of free hydrogen (much needed for welding, cutting and annealing). An engineering works *could* buy its hydrogen as compressed gas, but the weight of the containing cylinders would make carriage charges very heavy. An equal weight of hydrogen, present in liquid ammonia, can be conveyed at far less cost. To be precise, in conveying 3 lb. of compressed hydrogen, the *total* weight to be moved is the same as in conveying 200 lb. of liquid ammonia, containing more than 35 lb. of combined hydrogen.

At the works the ammonia is 'cracked' by heating to about 930° C., giving a mixture containing 75 per cent. of hydrogen by volume. For most purposes the 25 per cent. of nitrogen is not detrimental.

A certain amount of ammonia (in solution) is used for cleaning purposes.

By far the greater part of all the ammonia manufactured, however, is turned into the sulphate—in gas-works, for instance, as already described—and sold as a fertilizer. This subject—the use of ammonia as a fertilizer—is so important that we shall consider it in some detail in Chapter 32.

Questions

N.B. *See note in italics,* p. 132

1. How would you use ammonium chloride to obtain a few jars of dry ammonia gas?

State briefly how this gas is obtained on a large scale. How would you demonstrate (*a*) that it is very soluble in water; (*b*) that its solution has some properties similar to those of sodium hydroxide solution? *Lond.*

2. Draw labelled diagrams to show the apparatus and materials required to prepare (*a*) several jars of dry ammonia; (*b*) an aqueous solution of ammonia.

Describe and explain what you would observe if gaseous ammonia were (i) passed over heated copper oxide; (ii) mixed with hydrogen chloride; (iii) added to chlorine water; (iv) mixed with air or oxygen and passed over heated platinised asbestos. *Lond.*

3. What volume of ammonia is required to combine with 23·7 c.c. of hydrogen chloride, all volumes being measured at room temperature and pressure?

4. Dry ammonia was passed over a weighed quantity of copper oxide (cf. fig. 28/2). The water produced was arrested by a weighed U-tube containing quicklime, and the nitrogen which passed on was collected over water. 1·215 gm. of water was produced, and the volume of nitrogen after being reduced to N.T.P. was 500 c.c. The copper oxide lost weight by 1·08 gm.

Find the percentage composition of ammonia by weight, and the simplest formula. What further information would you need to obtain the molecular formula?

5. If a stream of ammonia is passed through a red-hot tube the gas can then be burnt in air. How do you account for this?

6. How does ammonia react with (*a*) water; (*b*) copper oxide? *O.C.* (*part*)

7. Ammonia is sometimes described as 'the anhydride of a base.' Justify this description.

8. Ammonium chloride is said to 'sublime' and also to 'dissociate' when heated. What do you understand by these terms? How would you demonstrate the first phenomenon with regard to ammonium chloride?

Describe the preparation and the collection of dry ammonia, giving also a labelled sketch of the assembled apparatus.

Briefly state how ammonia is obtained from the products of coal distillation. *Brist.*

9. Find the simplest formula of a substance whose percentage composition is nitrogen 35, hydrogen 5 and oxygen 60. What is this substance?

10. Explain how you would test a given solid to find out if it contained any ammonium salt. What is the importance of ammonium salts in the soil? *Camb. (part)*

11. What volume of hydrogen could be obtained from 60 c.c. of ammonia, both gases being measured under the same conditions of temperature and pressure?

12. (i) When an excess of saturated ammonia solution was added to 120 c.c. of chlorine the chlorine disappeared and 40 c.c. of nitrogen was produced. (ii) Dry ammonia was found to have a density, relative to hydrogen, of 8·5. From these two items of information deduce the formula of ammonia, pointing out clearly any assumptions you make.

13. In the manufacture of 'synthetic ammonia' from nitrogen and hydrogen, we have examples of (i) a reversible reaction, (ii) chemical equilibrium, and (iii) the use of a catalyst. Write a short account of the process so as to bring out the features just mentioned.

The higher the temperature, the more quickly is equilibrium obtained. Why, then, is the temperature limited to the comparatively low one of 500° C. or so?

14. Give some account of the chief uses of ammonia.

CHAPTER 29

NITRIC ACID AND NITRATES

Sodium Nitrate. We shall begin with this substance, because until comparatively recently it was the raw material from which all nitric acid was made; and even to-day very large quantities of it are used for that and other purposes.

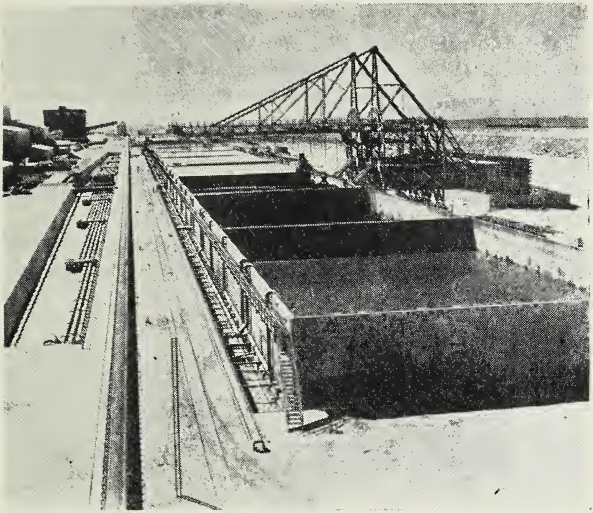
It was mentioned in the Introduction (p. 2) that this important substance occurs naturally in Chile, whence its commercial name 'Chile saltpetre.' The deposits cover an area of about 344 sq. miles in a desert region in the north of the country. The district is nearly rainless—in fact, as sodium nitrate is very soluble in water, it is evident that it would long since have been washed out of the soil if there had been any great amount of rain. But how were these deposits formed?

According to one theory, the 'caliche' (as the crude substance is called) is derived from guano—the droppings of sea-birds. But in that case it should contain a considerable proportion of phosphates, and it does not.

Another theory has it that northern Chile was once under the sea, and that immense quantities of seaweed were present. Earth movements caused the sea-bed to be raised to its present level, and by bacterial action the weed was converted into caliche. In support of this idea is the fact that the deposits contain an appreciable quantity of iodine (as sodium iodate), an element commonly associated with seaweed. There are other theories, but nobody yet can answer the question with certainty.

The caliche is usually found a few feet below the surface. Bore-holes are made and gunpowder or dynamite cartridges introduced. The explosion makes the substance far more accessible. It is then crushed and treated with boiling water, the insoluble constituents (sand, etc.) being allowed to settle. After this, the solution is run off into enormous tanks in which the sodium nitrate crystallises out as the liquid cools. The illustration shows a series of ten such tanks, each of 11,400 tons capacity, in which these operations are carried out. On the left can be seen the rubber conveyor belt which conveys the crushed caliche from the crushing plant to the tanks. It is a yard wide and more than a mile long—one of the longest conveyor belts in the world.

The export of Chile saltpetre began in 1830 with 1000 tons, and had risen by 1911 to about 2½ million tons. The world's demand for 'fixed nitrogen' (chiefly as ammonium salts and nitrates) is still rapidly on the increase. That increase, however, is being met chiefly by the production of synthetic products, as explained in Chapter 28, and there has consequently been less demand for the South American product.



By courtesy of The Chilean Iodine Educational Bureau

Tanks for extracting soluble matter from caliche

The Chilean Government formerly raised something like three-quarters of its entire revenue by levying a tax on every ton of nitrate exported, so it must have suffered heavy losses through the competition of the synthetic compound, We have seen how Chile saltpetre is used as a fertilizer. We will now consider its use in making nitric acid.

(For the effect of heat on sodium nitrate, see p. 340.)

Nitric Acid. In the laboratory, nitric acid is made by putting a handful of sodium (or potassium) nitrate in a retort, covering it with concentrated sulphuric acid and heating:—

$$\mathrm{NaNO_3 + H_2SO_4 = NaHSO_4 + NHO_3}$$

(or $$\mathrm{KNO_3 + H_2SO_4 = KHSO_4 + HNO_3})$$

The nitric acid produced has a much lower boiling-point than sulphuric acid. It therefore distils over into a receiver, R, while any excess of sulphuric acid remains behind in the retort.

On the large scale, a certain amount of nitric acid is still made by the reaction just described, especially in localities which are very favourably situated for the import of Chile saltpetre. A much larger amount, however, is prepared by the oxidation of ammonia. The chemical changes that take place will be understood better after the oxides of nitrogen have been studied, so we will postpone further treatment to our next chapter.

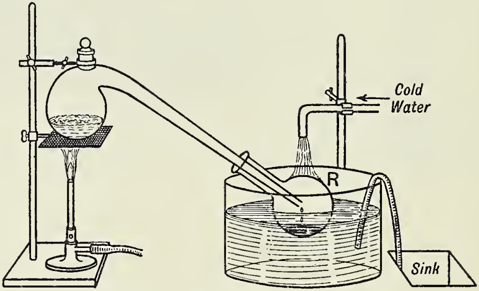


FIG. 29/1. Preparation of nitric acid

Properties. Nitric acid shows two distinct sets of properties

(i) Those of an *acid*.

(ii) Those of an *oxidising agent*.

As an acid it turns litmus paper red, and forms salts when it acts upon a metal, or upon the oxide, hydroxide or carbonate of the metal (cf. p. 153). Thus it acts upon copper oxide to produce copper nitrate, upon calcium carbonate to produce calcium nitrate and so on:—

$$CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O$$
$$CaCO_3 + 2HNO_3 = Ca(NO_3)_2 + H_2O + CO_2$$

In these ways the action of nitric acid is very similar to that of hydrochloric or sulphuric acid, the only difference being that nitrates are formed instead of chlorides or sulphates. There is one very marked difference, however. When a metal dissolves in dilute hydrochloric or sulphuric acid, *hydrogen* is given off (you will remember that this gas is usually prepared by dissolving zinc in one or other of these acids, as described on p. 111). *With nitric aid this is hardly ever the case.* This is because nitric acid is an oxidising agent. Quite possibly hydrogen is produced at first, but before it has had a chance to escape it is seized upon by the oxygen in the acid and converted into water.

Magnesium is an exception to the general rule, for with very dilute nitric acid hydrogen *is* obtained. Let us try to see why. We can readily show by experiment that magnesium causes hydrogen to be given off very freely when greatly diluted sulphuric or hydrochloric acid is used. No doubt the same thing happens with nitric acid, and the bubbles come off so freely that they reach the surface before the nitric acid, in its highly diluted state, is able to oxidise them completely.

However, let us leave the exception and go back to the general rule.

It is easy enough to see what happens to the hydrogen that has been oxidised by the nitric acid, but what happens to the nitric acid that has been reduced by the hydrogen?

When studying the reduction of sulphuric acid (H_2SO_4) we saw that it was convenient to regard it as $H_2O{\cdot}SO_3$. The reducing agent removes some of the oxygen, leaving $H_2O + SO_2$. Occasionally, the reducing agent removes the whole of the oxygen, leaving H_2S.

In the same way it will be convenient for us to regard nitric acid as $H_2O{\cdot}N_2O_5(=2HNO_3)$. What will be formed when the N_2O_5 is reduced?

Now sulphur forms only *one* oxide lower than SO_3. Hence on reduction we could be sure that this one (the dioxide, SO_2) would be produced. Nitrogen, however, forms *four* oxides lower than the pentoxide N_2O_5. They have the formulæ N_2O_4 (or NO_2), N_2O_3, NO and N_2O. The reduction of nitric acid, therefore, gives rise to far more complications than the reduction of sulphuric acid. Again, just as by the reduction of sulphuric acid a compound of *sulphur* and hydrogen (H_2S) is sometimes formed, so on the reduction of nitric acid a compound of *nitrogen* and hydrogen (NH_3) is occasionally formed. This compound—ammonia—we have already studied. You will not expect to find ammonia *given off* in any reaction where nitric acid is concerned, because it would at once combine with the acid, forming ammonium nitrate.

It seems, then, that when nitric acid is reduced we may have formed one or more of four different oxides, and that ammonia (becoming ammonium nitrate) may also be produced. Such possibilities make the stoutest heart quail. Luckily, one of these four substances is produced much oftener than any of the others, and at this stage we shall not need to worry much about the remaining three. The one that is so often produced is a reddish-brown gas known as nitrogen dioxide (NO_2).

Again and again we shall find, in using nitric acid, that dense brown fumes are produced. This is always a sign that the nitric acid is being reduced and therefore, of course, that the substance with which it is in contact is being oxidised. We will now consider one or two examples of this. The best results will be obtained by using the nitric acid you have made yourself. The nitric acid in the bench bottles is not quite so concentrated in spite of its label.

Warm dry sawdust takes fire when nitric acid is poured on it. It is easy to understand what happens. Sawdust contains a high proportion of the element carbon. The nitric acid oxidises this to carbon dioxide, and the chemical action is so vigorous that it is accompanied by flame.

When nitric acid is poured on phosphorus the latter burns brilliantly, dense fumes of phosphorus pentoxide being produced. The liquid left behind is found to contain *orthophosphoric acid*, H_3PO_4, which may be regarded as $P_2O_5 + 3H_2O(=2H_3PO_4)$. Both in this case and in the preceding one reddish-brown fumes of nitrogen dioxide are seen, showing that the nitric acid is undergoing reduction.

Having in mind the cases of carbon and phosphorus, we can almost guess what would happen if nitric acid were heated with sulphur. We should expect (i) that the sulphur would be *fully* oxidised, i.e. to sulphur trioxide, SO_3, and (ii) that this oxide would combine with any water originally present (or produced by the reduction of nitric acid) forming sulphuric acid. In short, we should expect the final products to be nitrogen dioxide and sulphuric acid, and this is found to be the case.

If hydrogen sulphide is passed through cold nitric acid (slightly diluted), the hydrogen is oxidised and the sulphur set free (cf. p. 309) $(2HNO_3 + H_2S = S + 2H_2O + 2NO_2)$.

We must now consider the action of nitric acid on hydrochloric acid. In Chapter 22 we studied a number of cases in which the latter was heated with an oxidising agent (e.g. manganese dioxide) and found that the result was always the same—the hydrogen in the acid was oxidised to water and the chlorine was set free.

Using nitric acid as the oxidising agent, we find that chlorine is produced as usual, but an orange-coloured gas called *nitrosyl chloride*, NOCl, is formed at the same time. The equation is

$$HNO_3 + 3HCl = 2H_2O + NOCl + Cl_2$$

This mixture of nitric and hydrochloric acids is known as *aqua regia*. The name means 'royal liquid,' and was used by the alchemists because they found that this acid mixture would dissolve gold, the 'king of metals.' The gold goes into solution as the chloride, $AuCl_3$. Aqua regia will also dissolve platinum.

Nitric acid alone will not dissolve gold, and neither will hydrochloric acid. The reason why aqua regia should be so effective is not fully understood, but the result is due at least in part to the production of chlorine. In support of this is the fact that gold is slowly dissolved by a solution of chlorine in water.

When nitric acid is poured on copper, zinc, iron—almost any metal, in fact—we obtain the same brown fumes we have so often noticed before. You would not expect to find the *oxide* in any of these cases, because in contact with nitric acid the oxide would become a *nitrate.* With copper oxide, for instance, we should have

$$CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O$$

We will conclude our account of nitric acid as an oxidising agent by describing an experiment which shows that it *contains oxygen* (as we saw on p. 279, an oxidising agent does not always contain oxygen—chlorine is a case in point).

A churchwarden pipe, ABC, is clamped in the position shown in fig. 29/2, and at C a short bend of glass tubing is attached (inside the rubber, the glass tubing must actually *touch* the pipe; otherwise the rubber is very quickly destroyed).

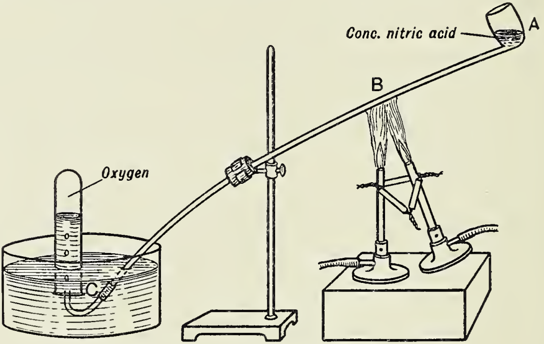


FIG. 29/2. Oxygen from nitric acid

The pipe is now strongly heated at B by means of a bunsen, —two bunsens if possible—and about 5 c.c. of concentrated nitric acid is poured into the bowl. In passing the heated portion it is decomposed, and oxygen is collected in the test-tube. Brown fumes are seen inside the glass bend, but they are evidently very soluble, for they do not collect in the tube.

Uses of Nitric Acid. The chief use of nitric acid is in the manufacture of fertilizers, including sodium nitrate (made by treating soda ash with the acid). Other uses are in the manufacture of explosives, dyes, drugs and artificial silk.

Although as already mentioned, we shall postpone for a little while an account of the present-day method of manufacturing nitric acid, this is perhaps the best place in which to point out its possibilities for good and evil. They are summed up in two words that occur in the preceding paragraph—'fertilizers' and 'explosives.'

We are no longer dependent on Chile for supplies of nitrate. By modern methods, nitric acid can be made on an unlimited scale, practically from air and water; and the acid has only to be neutralised, with say chalk or soda, to give us all the nitrates we need. We no longer have to fear the prospect of famine arising from a soil starved of nitrogen fertilizers. That surely is cause for rejoicing.

But there is that other word 'explosives,' which, of course, have their peace-time uses; they have other 'uses' as well.

Before 1913 a country could manufacture explosives on the large scale only if it had access to the nitrate beds of Chile. Germany could not have gone to war, because the British Navy would have cut her off from those supplies.

But the modern process to which we have referred made her completely independent of imported nitrate, and we know what happened. It is sad to think that discoveries which have gone far to solve the world's great food problems also made possible two of the most devastating wars of all history.

Nitrates. We have already seen that to make a nitrate we must dissolve in nitric acid either a metal itself, or the oxide, hydroxide or carbonate of the metal. When solution is complete and we wish to obtain the solid nitrate, we must evaporate down very gently, on a water-bath for preference. The reason for this is that most nitrates readily decompose on heating, as we shall see presently.

When we were making nitric acid we added concentrated sulphuric acid to sodium (or potassium) nitrate. This indicates a general property of nitrates—*they yield nitric acid on treatment with concentrated sulphuric acid.*

This is the basis of a very useful test for nitrates. Put a little of the substance in a test-tube, warm it with a few drops of concentrated sulphuric acid and see if nitric acid is produced—coming off, no doubt, in the form of a vapour.

But how are we to tell if this *is* the vapour of nitric acid?

The simplest plan is to mix a little copper with the suspected nitrate before adding the sulphuric acid. As soon as the nitric acid is produced (from nitrate + sulphuric acid) it is reduced by the copper, and the familiar brown fumes make their appearance. We can express the result by two equations. Suppose, for instance, that calcium nitrate had been used. We have first the formation of nitric acid:—

$$Ca(NO_3)_2 + H_2SO_4 = CaSO_4 + 2HNO_3$$

and then the reduction of the nitric acid by the copper:—

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2H_2O + 2NO_2$$

We must next consider the *action of heat* on nitrates. All of them decompose, and in most cases the oxide of the metal remains, while nitrogen dioxide and oxygen are given off, e.g.

$$[Cu(NO_3)_2 = CuO + 2NO_2 + O]$$
$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$$

(We have here an excellent method for making the oxide of a metal. Dissolve the latter in nitric acid, making the nitrate. Then, after evaporating to dryness, heat the nitrate strongly. It decomposes, giving the oxide.)

Potassium and sodium nitrates decompose in an entirely different way. Oxygen is given off and a *nitrite* remains:—

$$[KNO_3 = KNO_2 + O]$$
$$2KNO_3 = \underset{\textit{Potassium nitrite}}{2KNO_2} + O_2$$

Lastly, ammonium nitrate when heated gives *nitrous oxide* and water:—

$$NH_4NO_3 = N_2O + 2H_2O$$

Gunpowder. If we melt some potassium (or sodium) nitrate in an evaporating dish and drop into it a piece of charcoal about the size of a pea, the charcoal soon glows and takes fire, and after a little while burns away completely.

A somewhat similar result is observed with sulphur. We saw above that the nitrate on heating gives off oxygen (leaving the nitrite). The carbon and sulphur combine with the oxygen, and are turned into carbon dioxide and sulphur dioxide respectively.

The formation of carbon dioxide plays an essential part in the action of gunpowder, a mixture consisting of about 75 per cent. of 'nitre' or 'saltpetre' (potassium nitrate), 13 per cent. of charcoal and 12 per cent. of sulphur. When the powder is exploded the carbon is suddenly converted into carbon dioxide at the expense of the oxygen contained in the saltpetre. The potassium gives rise to potassium sulphide, and nitrogen is set free (cf. Question **6** on p. 342). Now carbon dioxide and nitrogen at ordinary pressure would occupy an enormously greater volume than the carbon and saltpetre from which they are produced, and this volume would become greater still owing to the high temperature reached at the moment of explosion. All this gas, however, is contained within the limited space of a cartridge, and the result is that an immense pressure is exerted which drives the bullet out with terrific force.

Sodium nitrate is not used in gunpowder because, unlike potassium nitrate, it is somewhat hygroscopic (i.e. it absorbs moisture from the air). Thus gunpowder containing sodium nitrate would be damp.

The oxidising action of potassium nitrate is made use of in other ways. 'Touch-paper,' for instance, is made by soaking paper in a solution of the substance and then drying it. Perhaps you have seen one of those advertisement leaflets in which you are instructed to 'touch the spot marked * with a hot wire.' You do so, and the paper smoulders along a definite track. 'Puffman's Pills for Pimples,' or something like that. The characters have first been traced with a strong solution of nitre. You can easily do it for yourself. Choose a piece of thin paper with not much glaze.

Questions

N.B. *See note in italics*, p. 132

1. How, starting from sodium nitrate, would you prepare in the laboratory a sample of nitric acid? Give a diagram and the equation.

What is meant by *oxidation*? Describe *two* experiments, one (*a*) to show that nitric acid is an oxidising agent, and the other (*b*) to show that nitric acid is an acid. *J.M.B.*

2. Describe an experiment to show that nitric acid contains oxygen.

3. Make out a table of four columns headed respectively (i) Oxidising agent; (ii) Example of reaction; (iii) Oxidation product; (iv) Reduction product. In column (i) enter the four oxidising agents Oxygen, Hydrogen peroxide, Nitric acid, Chlorine, and complete the table. Column (ii) should include the equation representing the reaction.

4. Describe the preparation of nitric acid in the laboratory.

What substances are formed when nitric acid acts on (*a*) ammonia; (*b*) lead; (*c*) potassium carbonate?

State what you would *observe* and name the substances produced when each of the crystalline products from the three reactions is heated. *Brist.*

5. What happens when sodium nitrate is (*a*) heated alone; (*b*) warmed with concentrated sulphuric acid?

A solution containing 10 gm. of lead nitrate is mixed with excess of sodium chloride solution. Calculate (*a*) the weight of lead chloride formed; (*b*) the weight of sodium nitrate which would be produced. *Camb.*

6. The reaction which accompanies the explosion of gunpowder is believed to be expressed approximately by the equation $2KNO_3 + S + 3C = K_2S + N_2 + 3CO_2$. On this basis, what should be the percentage composition of gunpowder?

7. *An exercise in the writing of formulæ.*

In the table given on p. 343, valencies are indicated by the number of + or − signs.

Complete the table. Afterwards, underline the formula for each of the following: 1*st line*—Sodium chloride and carbonate. 2*nd*—Potassium nitrate. 3*rd*—Ammonium sulphate. 4*th*—Lead sulphide. 5*th*—Copper chloride. 7*th*—Ferrous sulphate and sulphide. 8*th*—Ferric nitrate. 9*th*—Aluminium sulphate. 10*th*—Zinc nitrate. 11*th*—Calcium carbonate.

Acid→ *Metal* ↓	*Chloride* Cl^-	*Nitrate* NO_3^-	*Sulphate* SO_4^{--}	*Carbonate* CO_3^{--}	*Sulphide* S^{--}
Sodium, Na^+					
Potassium, K^+					
Ammonium, NH_4^+					
Lead, Pb^{++}					
Copper, Cu^{++}					
Iron:					
Ferrous, Fe^{++}					
Ferric, Fe^{+++}					
Aluminium, Al^{+++}					
Zinc, Zn^{++}					
Calcium, Ca^{++}					

8. (i) Calculate the volume, at 15° C. and 74 cm. pressure, of the whole of the oxygen present in 126 gm. of nitric acid.

Making use of your answer, *write down* (ii) the volume of hydrogen and (iii) the volume of nitrogen present in the quantity mentioned, likewise at 15° C. and 74 cm. pressure.

CHAPTER 30

OXIDES OF NITROGEN

The Oxides of Nitrogen. We have already referred to the oxides of nitrogen, but we shall now study some of them in a little greater detail, dealing with nitrous oxide (N_2O), nitric oxide (NO) and nitrogen dioxide or peroxide (NO_2).

Nitrous Oxide. Nitrous oxide, N_2O, may be produced by reducing dilute nitric acid with zinc. It is much more conveniently prepared, however, by heating solid ammonium nitrate (the equation has already been given on p. 340). The nitrate soon melts, and a little while afterwards the gas begins to come off.[1] It should be collected over hot water, as it is rather easily soluble in cold.

The gas may contain a little nitric oxide (NO) as an impurity. This may be removed by first passing it through a Woulff bottle containing ferrous sulphate solution (cf. fig. 17/3). The action of this solution will be understood after nitric oxide has been studied.

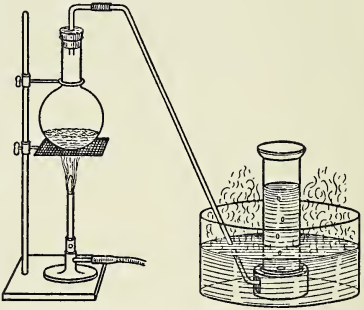


FIG. 30/1. Preparation of nitrous oxide

Nitrous oxide has a faint, rather sweetish taste and smell. If sulphur which is only just alight is plunged into the gas it is extinguished, but if properly alight it continues to burn with greatly increased brilliancy. The reason is that nitrous oxide, strictly speaking, is a non-supporter of combustion, and so it extinguishes the feebly burning sulphur. When the sulphur is well alight, however, it is sufficiently hot to *decompose* the nitrous oxide into nitrogen and oxygen, and then it continues to burn at the expense of the oxygen.

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[1] The nitrate must not be *very* strongly heated, or there is some danger of an explosion. On the other hand, the gas collected just above the melting-point often fails to re-ignite a glowing splint owing to the presence of much nitrogen.

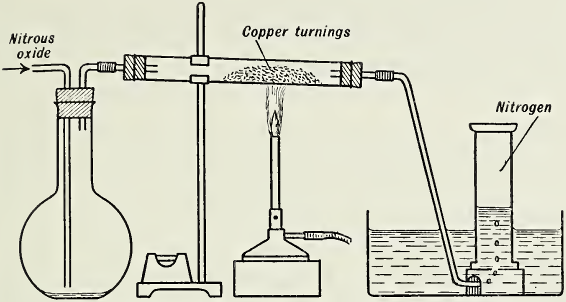


FIG. 30/2. Nitrogen from nitrous oxide

Even a glowing splint is sufficiently hot to bring about the same decomposition, and so will burst into a flame pretty much as it does in oxygen. Nitrous oxide, however, can easily be distinguished from oxygen by its greater solubility in water. We shall discover a *chemical* means of distinguishing the two gases when we come to study nitric oxide.

To show that nitrous oxide really contains both nitrogen and oxygen we pass the gas over heated copper. We can actually collect the nitrogen, and the fact that the copper is turned into copper oxide shows the presence of oxygen. The apparatus shown in fig. 30/2 may be used, the big flask serving to retain the steam which comes over with the nitrous oxide, and which might otherwise condense in the combustion-tube and crack it.

A similar method may be used to show the presence of nitrogen and oxygen in other oxides of nitrogen.

Nitrous oxide is largely used by dentists in the painless extraction of teeth. It has been called 'laughing gas,' because of the hysterical effect sometimes produced on the patient.

It is prepared industrially by heating very pure ammonium nitrate to 200° C. in retorts, great care being taken to remove any harmful impurities (e.g. it is passed through caustic soda solution to remove traces of nitric acid vapour). It is transported in steel cylinders, as a liquid, under a pressure of 100 atmospheres.

It was discovered by Priestley, but was first used as an anæsthetic by Sir Humphry Davy in 1799. He breathed sixteen quarts of it for 'near seven minutes,' and says that it made him 'absolutely intoxicated.' A risky experiment!

Nitric Oxide. Nitric oxide is formed by the action of somewhat diluted nitric acid on copper (take equal parts of water and concentrated acid). No heat is required. The gas may be collected over water. The equation is

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$$

It is a colourless gas, easily distinguished from all other gases by the fact that it turns brown on exposure to the air, nitrogen dioxide being formed

$$[NO + O = NO_2]$$
$$2NO + O_2 = 2NO_2$$

So nobody knows what nitric oxide smells like, because what we smell is always nitrogen peroxide.

We can use this reaction to distinguish between nitrous oxide and oxygen. The gas, contained in a jar or test-tube, is placed over water, and nitric oxide is slowly bubbled into it. If the gas is oxygen it will combine with the nitric oxide, forming the very soluble brown gas nitrogen dioxide, and the water will therefore rise. If the gas is nitrous oxide it will simply mix with the nitric oxide, and the level of the water will fall.

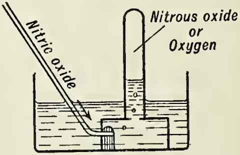


Fig. 30/3
Distinguishing nitrous oxide from oxygen

It is possible to find the percentage of oxygen in air by placing a measured volume of the latter in the jar, passing nitric oxide slowly into it, and shaking after each addition.

So long as any uncombined oxygen remains, brown fumes will form and the water will continue to rise. When it begins to *fall* it means that all the oxygen has been used up. The gas remaining in the jar is then nitrogen, and we have only to read its volume. We should not now agree with Dalton that this method for finding the composition of the atmosphere is 'the most elegant and expeditious of all.' However, in spite of the crudity of the method, he obtained a very good result, for he reports that 'the bulk of any given quantity of atmospheric air appears to be reduced nearly 21 per cent. by abstracting its oxygen.'

Feebly burning phosphorus is extinguished by nitric oxide, while brightly burning phosphorus burns with increased brilliance. The explanation is quite similar to that already given in connection with nitrous oxide.

When shaken up with ferrous sulphate solution, nitric oxide forms a dark-brown compound, which has the formula $FeSO_4 \cdot NO$. On heating, this readily decomposes into ferrous sulphate and nitric oxide, and hence we have a means of preparing very pure nitric oxide. The rather impure gas obtained by the action of diluted nitric acid on copper is passed through a solution of ferrous sulphate. The impurities pass on, but the nitric oxide remains behind, forming the dark-brown solution of which we have spoken. This solution is now transferred to a clean flask (fitted with delivery-tube, etc.) and heated, when pure nitric oxide is given off.

The formation of this brown compound also provides us with a useful test for a nitrate. The suspected nitrate is dissolved in water, and mixed with about an equal volume of ferrous sulphate solution in a test-tube. The tube is now tilted slightly, and concentrated sulphuric acid is poured down the side. The heavy acid sinks to the bottom of the test-tube, and where its surface touches the mixture (of nitrate + ferrous sulphate) a brown ring is observed. Its formation is explained in this way

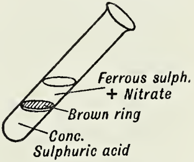


FIG. 30/4. The 'brown ring' test

(i) Nitric acid is produced by the action of sulphuric acid on the nitrate (cf. pp. 334, 340).

(ii) The nitric acid is *reduced* by the ferrous sulphate to nitric oxide.

(iii) Nitric oxide combines with more ferrous sulphate, forming the brown compound already discussed.

On shaking, the ring quickly disappears, because heat is produced as the sulphuric acid mixes with the water present, and the heat at once decomposes the brown compound.

Formula of Nitric Oxide. To show that the formula of nitric oxide is NO, apparatus similar to that shown in fig. 16/4 is used, but instead of the current passing through a piece of carbon it passes through (and heats to redness) a piece of thick iron wire about 3 inches long. The hot iron combines with the oxygen (of the nitric oxide), leaving the nitrogen. After the apparatus has cooled down to its original temperature it is found that the volume of the nitrogen is half that of the original gas,

i.e. 2 vols. of nitric oxide contain 1 vol. of nitrogen. (i)

Suppose 1 vol. of nitrogen contains n molecules.
∴ 1 ,, ,, nitric oxide ,, ,, ,, (AVOGADRO)
∴ 2 vols. ,, ,, ,, contain $2n$,,

∴ instead of (i) we may write

$2n$ molecules nitric oxide contain n mols. nitrogen. Cancel by $2n$.

∴ 1 mol. of nitric oxide contains $\frac{1}{2}$ mol. nitrogen $=1$ atom of nitrogen (assuming that the mol. of nitrogen contains 2 atoms).

∴ formula for nitric oxide is NO_x where x remains to be determined.

Now the density of the gas relative to hydrogen is found by experiment to be 15.

∴ mol. weight $=30$.

But the molecule contains 1 atom of nitrogen, of weight 14 (proved).

∴ wt. of oxygen $=30-14=16$, which is the weight of *one* atom of oxygen.

∴ the formula is NO.

A similar experiment may be carried out with nitrous oxide. In this case the volume of nitrogen left is *equal* to that of the original nitrous oxide. From this information, together with the fact that the density relative to hydrogen is 22, the student is invited to prove for himself that the formula must be N_2O.

Nitrogen Dioxide (often, but not very correctly, called 'nitrogen peroxide'—see p. 152). We have just seen that if nitric acid is somewhat diluted with water, copper will reduce it to nitric oxide. If, however, the nitric acid is not diluted at all, copper reduces it to *nitrogen dioxide*:—

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2H_2O + 2NO_2$$

The gas must be collected by displacing air upwards, as it is readily soluble in water (with chemical change, see p. 352). As in the preparation of nitric oxide, no heat is required.

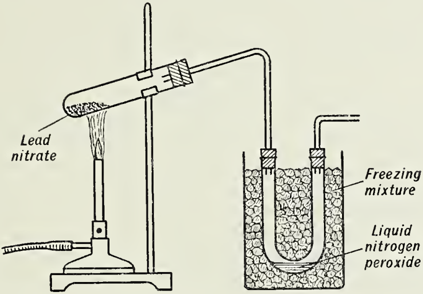


FIG. 30/5. Preparation of liquid nitrogen peroxide

Another way of making nitrogen dioxide is by heating lead nitrate in a test-tube:—

$$[Pb(NO_3)_2 = PbO + 2NO_2 + O]$$
$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$

If the gas thus produced is passed through a U-tube surrounded by a freezing mixture, *liquid* nitrogen dioxide is formed as a pale-yellow liquid. In practice the liquid produced is usually green, becoming yellow after standing for a while. The explanation seems to be that a small quantity of another oxide of nitrogen, the trioxide (N_2O_3) is present. Nitrogen trioxide is a blue liquid, and this blue, with the yellow of the nitrogen dioxide, gives green. As the temperature rises the trioxide decomposes ($N_2O_3 = NO + NO_2$). Nitric oxide escapes, and only the yellow nitrogen dioxide remains.

The reason why lead nitrate is chosen for the preparation of nitrogen dioxide is that it happens to contain no water of crystallisation. If *copper* nitrate, for instance, had been used, water of crystallisation would have been driven off as steam, and this would have reacted with the nitrogen dioxide in a way which will be described presently.

On gently warming liquid nitrogen dioxide it deepens in colour and boils at 22° C. Reddish-brown vapours are now given off, and these become darker and darker as the containing vessel is heated. It has been shown that this change of colour is accompanied by a chemical change of a rather curious kind. At low temperatures the gas is really *dinitrogen tetroxide*, N_2O_4. As the temperature is raised, the molecules begin to break up, nitrogen dioxide being formed ($N_2O_4=2NO_2$). This change goes on to a greater and greater extent, until at about 150° the gas consists entirely of molecules having the formula NO_2. On cooling down, the chemical change is reversed, i.e. $N_2O_4=2NO_2$. A decomposition which is reversed when the conditions (usually temperature or pressure) are changed is known as a ***dissociation***, or (if only temperature is concerned) a ***thermal dissociation***. As in the case of other reversible reactions, the equation representing such a change is usually written with two arrows pointing in opposite directions, thus:—

$$N_2O_4 \rightleftharpoons 2NO_2$$

How do we know that at low temperatures the gas is represented by the formula N_2O_4 and at high temperatures by NO_2? Chiefly by the vapour density. At 150° C., for instance, the gas is 23 times as heavy as an equal volume of hydrogen (also weighed at 150° C.). Thus its vapour density is 23, and therefore its molecular weight is 46, which agrees with the formula $NO_2(14+2\times16)$. At 27° C.—just above the boiling-point of the liquid dioxide—the density is 38·3, and therefore the molecular weight is 76·6. Now N_2O_4 would have a molecular weight of $2\times14+4\times16=92$. We conclude that at 27° the vapour consists *mainly* of molecules of N_2O_4 (mol. wt. 92) mixed with some molecules of NO_2 (mol. wt. 46). In fact, the percentage of N_2O_4 molecules in the mixture at any temperature can be calculated from the vapour density—at 27° C. it works out to 80 per cent. (cf. Question 11 on p. 356). The condition is one of *equilibrium* such as we discussed in Chapter 9. Molecules of N_2O_4 are constantly breaking up into NO_2, and at the same rate molecules of NO_2 are constantly recombining to form N_2O_4. The result is that (for a given temperature and pressure) the mixture has a constant composition such as the one we have already noticed at 27° C. It is by no means always true, of course, that a chemical change is reversed when the conditions are reversed. When potassium chlorate is heated, for instance, it decomposes into potassium chloride and oxygen, but on cooling down, the potassium chloride shows not the slightest tendency to recombine with oxygen. Hence, though we say that the potassium chlorate *decomposes*, we do not say that it *dissociates*.

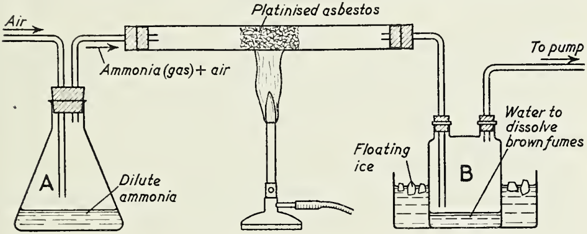


FIG. 30/6. Catalytic oxidation of ammonia

The behaviour of nitrogen dioxide towards burning substances is similar to that of other oxides of nitrogen we have studied, i.e. it is in itself a non-supporter of combustion, but if the temperature of the burning substance is sufficiently high, it is decomposed into nitrogen and oxygen, and the latter gas then enables the substance to continue burning.

Oxides of Nitrogen from Ammonia. We have already had examples of the reaction of ammonia with oxygen. Fig. 28/2 (p. 315) illustrates an experiment in which the oxygen is derived from copper oxide, and the ammonia is converted into nitrogen and water. The same products are obtained (though not so easily collected) when ammonia is simply *burnt* in an atmosphere of oxygen. In neither case was the *nitrogen* converted into an oxide.

In the presence of heated platinum, however, an oxide of nitrogen, nitric oxide, is actually formed. The experiment is illustrated in fig. 30/6. The platinised asbestos is first heated to redness, and then the suction pump is turned on. Brown fumes of nitrogen dioxide appear in the Woulff bottle and are easily dissolved in the water. There is reason to believe (though this experiment does not show it) that nitric oxide was first formed, afterwards combining with atmospheric oxygen to form the dioxide:—

$$[2NH_3 + 5O = 2NO + 3H_2O] \quad 4NH_3 + 5O_2 = 4NO + 6H_2O \qquad (a)$$

followed by $$2NO + O_2 = 2NO_2 \qquad (b)$$

If *A* is now pushed down into the liquid, the ammonia-air mixture becomes richer in ammonia, and instead of brown fumes appearing in the bottle, we get white ones, of ammonium nitrate and nitrite. The reason for this will be seen in the next paragraph.

Nitrous Acid and Nitrates. After dissolving the brown fumes of nitrogen dioxide, the water in the bottle B is found to be acid to litmus, chalk, etc. It contains a mixture of nitric and nitrous acids:—

$$2NO_2 + H_2O = HNO_3 + HNO_2 \qquad (c)$$

Nitrous acid is, however, very unstable, and easily breaks up on a slight rise of temperature, nitric acid and nitric oxide being formed:—

$$3HNO_2 = HNO_3 + H_2O + 2NO \qquad (d)$$

Thus the *final* result of passing nitrogen dioxide into water is that nitric acid and nitric oxide are produced.

The last equation but one will help us to see what happens when nitrogen dioxide is passed into a solution of sodium hydroxide (NaOH). We may suppose that nitric and nitrous acids are first formed, as already mentioned ($2NO_2 + H_2O = HNO_3 + HNO_2$), and that these are at once neutralised by the sodium hydroxide, forming sodium nitrate and nitrite:—

$$HNO_3 + NaOH = NaNO_3 + H_2O$$
$$HNO_2 + NaOH = NaNO_2 + H_2O$$

Adding 'partial equations' together, and subtracting the terms which are common to both sides, we get

$$2NO_2 + 2NaOH = NaNO_3 + NaNO_2 + H_2O$$

Using ammonium hydroxide (NH_4OH) instead of sodium hydroxide, we should, of course, have obtained a mixture of ammonium nitrate and nitrite, and that is why we got white fumes when the tube *A* was pushed down into the ammonia in our experiment (fig. 30/6). The necessary water was present in the form of vapour.

It will be convenient here to say a little more about nitrites. The last equation includes the formula for sodium nitrite, $NaNO_2$. We have met with this salt before—it is formed by strongly heating the nitrate (p. 340). On adding dilute hydrochloric or sulphuric acid to a *cold* solution, the unstable *nitrous acid* is produced ($NaNO_2 + HCl = NaCl + HNO_2$). We have already seen that with a slight rise of temperature this acid breaks up, giving rise to nitric acid and nitric oxide. The latter, of course, forms brown fumes on contact with air.

Thus a nitrite is easily distinguished from a nitrate by the fact that on adding a dilute acid, brown fumes are produced. Another test for a nitrite would be to mix its solution with ferrous sulphate solution and add a few drops of dilute acid. The solution turns brown because (i) nitrous acid is liberated, (ii) this decomposes, nitric oxide being one of the products, and (iii) the nitric oxide reacts with ferrous sulphate as mentioned on p. 347.

A solution of *ammonium nitrite* (in practice, a mixture of solutions of ammonium chloride and sodium nitrite) readily yields nitrogen on heating, and so is sometimes used in preparing this gas—$NH_4NO_2 = 2H_2O + N_2$. (Cf. the fact that ammonium *nitrate*, with an extra atom of oxygen, gives rise to nitrous oxide, N_2O.)

Nitric Acid from Ammonia. In our chapter on Nitric Acid we mentioned that this substance is chiefly manufactured from ammonia. We did not then describe the process, because to understand it some knowledge of nitric oxide and nitrogen dioxide is required, and we had not then studied these gases.

We have already discussed the chemical changes involved. They are summed up in equations (*a*), (*b*), (*c*), (*d*) on p. 352.

In the process of manufacture, catalytic oxidation is carried out by passing air mixed with about 10 per cent. of ammonia through several layers of platinum gauze of silk-like fineness, heated to 750° C. The process is remarkably efficient. The ammonia–air mixture is passed over the gauze at such a rate that it is in contact with it for only about $\frac{1}{500}$th of a second, and yet 96 per cent. of the ammonia undergoes oxidation.

The product is now cooled to promote combination of nitric oxide with oxygen.

Equation (*c*) represents the reaction of nitrogen dioxide with water, followed by decomposition of the nitrous acid (*d*). The manufacturing process is carried out in an absorption tower of stainless steel (acid resisting). The ascending gases meet a descending stream of dilute nitric acid, and react with the water present in it.

From (*d*) we see that some nitric oxide is present in the final products (theoretically, one-third of that originally formed from the ammonia). This is made to go through the cycle of changes again, still further reducing the amount, and so on.

It may be mentioned here that atmospheric nitrogen was first used in the large-scale manufacture of nitric acid at Notodden (Norway) in 1905. The process consisted in passing air through the flame of an enormous electric arc, when a small proportion (5 per cent. or so) of the nitrogen and oxygen combined to form nitric oxide. This was turned into nitric acid by the chemical changes we have already discussed.

The process was abandoned in 1928 in favour of the far more economic one in which ammonia is first synthesised (Haber–Bosch process) and then submitted to catalytic oxidation. By 1928 Norway, using the arc process, was converting 30,000 tons of nitrogen per annum into nitric acid and derived compounds. In 1955, by the new method, the amount was over 200,000 tons.

Questions

N.B. *See note in italics*, p. 132

1. Making use of the Index, write a short account of the work of Priestley.

2. Describe how you would prepare and collect some nitrous oxide gas. State *three* differences between this gas and oxygen.

Calculate the weight of the solid residue obtained when 10 litres of nitrous oxide measured at N.T.P. are passed over 50 gm. of heated copper. *Camb.*

3. A compound X has the following composition: Hydrogen = 5·0%, Oxygen = 60·0%, Nitrogen = 35·0%. (Atomic weights: N = 14·0; O = 16·0.) Calculate the simplest formula for X.

When the compound X is heated it gives a colourless gas whose vapour density is 22.

When the compound X is heated with sodium hydroxide it gives a colourless gas whose vapour density is 8·5.

What is the compound X? Give your reasons. *J.M.B.*

4. Sketch and label, without further description, an apparatus for preparing and collecting nitric oxide in the laboratory.

What happens when this gas is (*a*) exposed to air; (*b*) shaken with air and water; (*c*) passed into ferrous sulphate solution?

When passed over red-hot iron, nitric oxide is reduced and leaves half its volume of nitrogen. Given that its vapour density is 15, deduce its molecular formula. *Oxf.*

5. 0·621 gm. of an oxide of nitrogen yielded 0·290 gm. of nitrogen when heated with iron. Deduce the formula of the oxide of nitrogen. *Camb.* (*part*)

6. Nitric oxide combines with ferrous sulphate in solution to form a brown compound. Show how this reaction plays an important part (i) in testing for a nitrate; (ii) in preparing *pure* nitric oxide.

7. When burning phosphorus is plunged into a jar of nitric oxide it is sometimes extinguished, but sometimes burns more brightly. Explain.

8. Explain the meaning of the following terms: (a) *reversible reaction*, (b) *thermal decomposition*, and (c) *thermal dissociation*.

Describe any experiment you have seen to demonstrate thermal dissociation.

What happens when (i) lead nitrate, (ii) mercuric oxide, (iii) nitrogen dioxide, (iv) ammonium chloride are heated? In each case state to which class (or classes) of those given above the reaction belongs, giving your reasons. *J.M.B.* (*Alt.*)

9. Starting from lead and nitric acid, outline a method of obtaining samples of nitrogen dioxide (peroxide) and oxygen. Describe and explain the changes which take place when nitrogen dioxide is heated from room temperature to about 140° C.

How would you show that nitrogen dioxide contains nitrogen and oxygen?

What would be formed when a weak and cold aqueous solution of nitrogen dioxide is neutralised by ammonium hydroxide? What would you expect to happen if this neutralised solution were boiled for a short time? *Scot. L.C.*

10. Describe how you would obtain a sample of nitric acid from sodium nitrate. Give a sketch of the apparatus you would use.

State briefly how this acid is obtained on a commercial scale from ammonia.

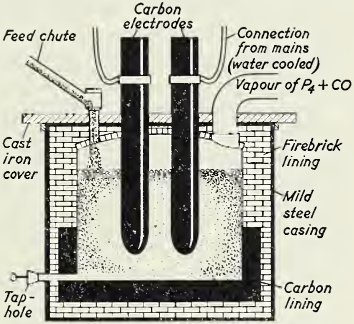
State very briefly, without sketches, how you would obtain from nitric acid samples of (*a*) oxygen; (*b*) nitric oxide; (*c*) nitrogen tetroxide, N_2O_4. *Lond.*

11. It has been found that at 60·2° C. 'nitrogen dioxide' (actually a mixture of molecules N_2O_4 and NO_2, p. 350), has a vapour density [$H=1$] of 30·1. Calculate: (i) the percentage of N_2O_4 molecules in the mixture at this temperature, and (ii) the percentage when the temperature is 100·1° C., given that at this temperature the vapour density has been found to be 24·3.

CHAPTER 31

PHOSPHORUS

Occurrence and Extraction. Phosphorus oxidises so readily that it could hardly occur in Nature in the free condition. The most important compound occurring naturally is calcium phosphate, $Ca_3(PO_4)_2$. This is found in many parts of the world as *phosphate rock*, where it is usually associated with calcium fluoride, CaF_2. Specially important localities are Florida and North Africa (whence European countries obtain the greater part of their supplies). Calcium phosphate occurs in bones to the extent of about 58 per cent. When these are strongly heated in air[1] organic matter burns away, and the *bone ash* which remains contains about 83 per cent. of calcium phosphate.



By courtesy of Messrs. Albright & Wilson Ltd

FIG. 31/1. Manufacture of phosphorus by the electric furnace

Very large amounts of phosphorus are extracted from phosphate rock by means of the electric furnace. The process is illustrated in fig. 31/1. A mixture of the crushed rock with sand and coke is fed into the furnace, which is raised to a very high temperature by an electric arc struck between the carbon electrodes. (Furnaces in use in England may consume as much as 8000 kilowatts—say 40,000 amps. at 200 volts.)

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[1] This would be a rather wasteful proceeding. Actually the bones are first heated in a retort out of contact with the air, when *animal charcoal* is produced (cf. the conversion of coal into coke). The animal charcoal is used for decolorising crude sugar, and it is not until it is 'spent' that it is strongly heated in air, leaving bone ash.

A convenient laboratory method of extracting calcium phosphate from bones is described on p. 174 of the author's *School Course of Practical Chemistry* (Bell).

Phosphorus vapour mixed with carbon monoxide passes out through a special contrivance for removing the dust, after which the phosphorus vapour is condensed to a liquid by sprays of warm water, while the carbon monoxide passes on, and is used as a fuel or in other ways.

The molten phosphorus is finally collected under water in a double-walled container. It may be conveyed as a liquid through steam-jacketed pipes to other parts of the works for immediate use, or to double-walled, 24-ton tanks of stainless steel, for rail transport.

Molten calcium silicate collects at the bottom of the furnace, and is run off from time to time through the slag-hole. Let us now try to understand the chemical changes that take place.

We may regard calcium phosphate, $Ca_3(PO_4)_2$, as being $3CaO + P_2O_5$ (basic oxide + acidic oxide). Sand contains the acidic oxide silica, SiO_2. The SiO_2 competes with the P_2O_5 for possession of the CaO, and competes successfully, because at the high temperature of the furnace, phosphorus pentoxide is volatilised, while silica is not. Thus we have

$$(3CaO)\cdot P_2O_5 + 3SiO_2 = 3(CaO\cdot SiO_2) + P_2O_5$$

or

$$Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5 \quad . \quad \text{(i)}$$

The phosphorus pentoxide is now reduced by the hot coke:—

$$P_2O_5 + 5C = 5CO + 2P \quad . \quad . \quad . \quad \text{(ii)}$$

Adding (i) and (ii), and cancelling P_2O_5, which comes on both sides, we obtain the complete equation

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C = 3CaSiO_2 + 5CO + 2P \quad . \quad \text{(iii)}$$

The manufacture of phosphorus is carried out at various places where cheap electric power is available. Its chief use is as the starting point from which are made the phosphates largely used in laundry work and in the preparation of baking powder. Smaller quantities are converted into red phosphorus for use in the match industry. In America very large amounts are used in making 'triple superphosphate' (p. 365).

World output of phosphorus has increased from about 5,000 tons a year in 1930 to some *sixty times* that amount at the present time—a clear indication that important new uses have been found for it.

Two Forms. Phosphorus is a pale yellow solid (colourless if very pure), with a crystalline appearance when broken across. Before dealing further with its properties, we will see how it can be turned into an allotropic form known as *red phosphorus* or *amorphous phosphorus.*

This change takes place when yellow phosphorus (or *white* phosphorus as it is often called) is heated to a special temperature—about 250°—in an atmosphere of nitrogen or carbon dioxide. It takes place more readily in the presence of a trace of iodine, which acts as a catalyst. The apparatus shown in fig. 31/2 on p. 361 (for the converse experiment) may be used. Air is first displaced from the test-tube by carbon dioxide, and a bit of phosphorus the size of a pea is placed at the bottom. Half an inch above this, with the help of a glass rod, a tiny crystal of iodine is placed. The cork with tube is now replaced, and after passing a little more carbon dioxide the phosphorus is heated for a few seconds with a good flame, which is removed as soon as the phosphorus has completely sublimed. In this experiment there will not be much escape of vapour from the upper tube. The sublimate is found to consist of the red variety. It can be touched with a fairly hot glass tube (below 200°) without taking fire.

On the large scale iodine is not used, but molten white phosphorus is run into an iron pot (beneath water) through a steam-heated pipe. When full, the pot is closed and electrically heated. The space above the phosphorus fills with steam, so that not much phosphorus burns. The temperature is maintained at 270° C. for several days, and is then raised to 400° C. to distil off any unchanged white phosphorus.

Properties. We will deal first with yellow phosphorus. Phosphorus means 'light bearer,' and it was so called because the men who first examined it were chiefly impressed by the fact that it glowed in the dark. Readers of *The Cloister and the Hearth* will remember that this property is the basis of a very exciting 'robber' scene, but here the author has gone astray, for the story deals with late fifteenth-century life, and phosphorus was not discovered till about 1670, by the physician Brand of Hamburg.

The glowing is the result of slow oxidation. On p. 78 we saw that this process is sufficient in the course of a few hours to remove the oxygen from the air contained in a glass vessel.

With a very slight rise of temperature phosphorus takes fire in air, giving off copious white fumes of phosphorus pentoxide, sometimes called *phosphoric oxide* ($P_4 + 5O_2 = 2P_2O_5$). Thus phosphorus is always kept under water, and must never (except when under water) be handled with the fingers. Phosphorus burns are very painful and take a long time to heal.

It is very soluble in carbon disulphide. If the solution is poured on a filter-paper the phosphorus takes fire as soon as the disulphide has evaporated.

This is because the phosphorus left behind is in a very finely divided condition, and so the total *area* at which phosphorus and oxygen are in contact is very large.

Yellow phosphorus is extremely poisonous, and is a common ingredient in the poisons used for rats and other vermin.

In contrast with the properties just mentioned, red phosphorus does not glow in the dark, and does not readily take fire in air (it has to be heated to about 240°). Thus it is quite safe to handle. When it *does* burn, however, the action is the same as already described. It is insoluble in carbon disulphide, and is non-poisonous. (Remember, however, that an ordinary sample of red phosphorus may contain a trace of the highly poisonous yellow variety.)

Red phosphorus has a higher specific gravity (2·20) than yellow (1·83). It consists of crystals so small that it was long thought to be amorphous; the crystalline structure of yellow phosphorus is well marked.

The contrast between the two forms stands out very clearly if some of their properties are summarised in a table (p. 361).

We have seen how yellow phosphorus may be converted into red. The opposite change is easily brought about by heating red phosphorus in an atmosphere of carbon dioxide,

White phosphorus	*Red phosphorus*
White, translucent.	Red, opaque.
Sp. gr. 1·83.	Sp. gr. 2·20.
Crystals easily seen.	Crystals extremely small.
Sol. in carbon disulphide.	Insol. in carbon disulphide.
Glows in the dark.	Does not glow.
Readily takes fire in air.	Does not readily take fire.
Easily attacked by hot solution of NaOH.	Not attacked by NaOH.
Very poisonous.	Non-poisonous.

as indicated in fig. 31/2. Drops of molten yellow phosphorus condense on the upper part of the tube.

(Incidentally, this experiment gives us an excellent example of the simplest type of flame, comparable with that of hydrogen or carbon monoxide. The zone of oxidation is in this case very obvious because the oxide of phosphorus is visible as a white smoke. In the case of, say, hydrogen, it is not obvious *to the eye* that the outer zone is one of oxidation.)

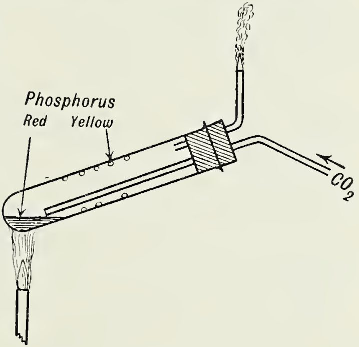

Fig. 31/2
Making yellow phosphorus from red

The evidence that red and yellow phosphorus are really the same element is similar to that which we discussed in connection with carbon and with sulphur. Thus, under suitable conditions

(i) Either form can be turned into *an equal weight* of the other.

(ii) By the oxidation of equal weights of the two forms we obtain equal weights of phosphorus pentoxide. Fig. 15/1 suggests a method by which the latter statement may be proved.

Phosphoric Acid. We have seen that when phosphorus is burnt, the *pentoxide* is produced.

We can easily prepare a small specimen by placing a fragment of phosphorus in a crucible which rests on a tile, and then setting fire to it by means of a hot wire. A bell-jar is placed over the top, and the dense fumes[1] of pentoxide settle as a white powder on the inside of the jar. If exposed to the air it soon becomes damp owing to absorption of moisture, which turns it into *metaphosphoric acid* (HPO_3):—

$$P_2O_5 + H_2O = 2HPO_3$$

Phosphorus pentoxide in fact is the most powerful drying agent we possess. So strong is its affinity for the elements of water that it can be used to obtain *anhydrides* from the corresponding acids. Thus if it is heated with sulphuric acid, sulphuric anhydride (i.e. sulphur trioxide) is obtained.

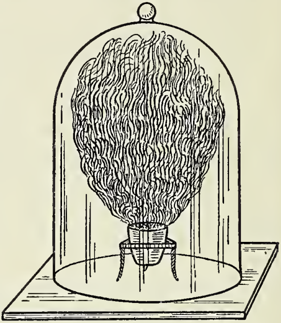

FIG. 31/3
Making phosphorus pentoxide

$$H_2SO_4 + P_2O_5 = 2HPO_3 + SO_3$$

Similarly nitric anhydride (N_2O_5) may be obtained from nitric acid.

When boiled with water, metaphosphoric acid is changed into orthophosphoric acid, H_3PO_4:—

$$HPO_3 + H_2O = H_3PO_4$$

A better way of making orthophosphoric acid is to oxidise red phosphorus by means of nitric acid, diluted with an equal volume of water to moderate the violence of the action.

$$5HNO_3 + P = H_2O + 5NO_2 + H_3PO_4$$

When the phosphorus has disappeared and the action has subsided, the solution is evaporated until the temperature rises to 180° C. The phosphoric acid remains as a thick, syrupy liquid which under rather special conditions may be made to deposit crystals.

---

[1] During World Wars I and II phosphorus was sometimes used for producing a smoke-screen.

To obtain the equation mentioned above we think of nitric acid, HNO_3, as $H_2O{\cdot}N_2O_5$, and of orthophosphoric acid, H_3PO_4, as $3H_2O{\cdot}P_2O_5$. We must also remember that the nitric acid is reduced to nitrogen dioxide, NO_2.

Now in becoming NO_2 (or rather $2NO_2$), $H_2O{\cdot}N_2O_5$ loses *one* atom of oxygen; but to become P_2O_5 two atoms of phosphorus must gain *five* atoms. Thus 2P must react with *five* times $H_2O{\cdot}N_2O_5$. This gives us

$$\begin{aligned} 5(H_2O{\cdot}N_2O_5) + 2P &= 5H_2O + P_2O_5 + 10NO_2 \\ &= (3H_2O + P_2O_5) + 2H_2O + 10NO_2 \end{aligned}$$

i.e. $$10HNO_3 + 2P = 2H_3PO_4 + 2H_2O + 10NO_2$$

Dividing through by 2, we obtain the equation already given.

Phosphoric acid may also be prepared by adding somewhat diluted sulphuric acid to calcium phosphate, keeping the mixture warm for a few hours, and then filtering to get rid of the calcium sulphate.

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$$

The filtrate may be concentrated by evaporation, but it contains a certain amount of monocalcium phosphate, $CaH_4(PO_4)_2$, a compound we shall be discussing presently.

Phosphates. Orthophosphoric acid is tribasic, i.e. it contains *three* hydrogen atoms which can be replaced by a metal. Thus it gives rise to *three* sodium salts having the formulæ NaH_2PO_4 (monosodium phosphate), Na_2HPO_4 (disodium phosphate) and Na_3PO_4 (trisodium phosphate) respectively. The word *orthophosphate* is nearly always shortened to *phosphate,* and disodium phosphate is so much commoner than the other two salts that it is usually referred to as *sodium phosphate.* It crystallises with $12H_2O$, and may be prepared by adding a solution of caustic soda to one of orthophosphoric acid until the indicator phenolphthalein is just turned red. The solution readily yields fine large crystals.

Comparing the salts of formulæ Na_3PO_4, Na_2HPO_4 and NaH_2PO_4, we may notice that in solution the first is strongly alkaline, the second faintly alkaline and the third definitely acid. This is in line with what we noticed about sodium carbonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$)—the 'hydrogen' salts are more acid (or less alkaline) than the normal ones.

These sodium phosphates have important uses. Because of its acidity, the monosodium salt NaH_2PO_4 is much used in baking powder, the other active constituent being sodium bicarbonate (cf. p. 179). The disodium and trisodium salts are often used in laundry work as constituents of washing powders, and of various 'detergents.' Let us try to understand their mode of action.

On p. 182 we saw that by adding sodium carbonate to hard water the calcium is precipitated as *carbonate*, leaving the water soft. Sodium triphosphate acts very similarly, the precipitate in this case consisting of calcium *phosphate*.

But now let us turn to another phosphate, sodium metaphosphate $NaPO_3$ (the sodium salt of the metaphosphoric acid mentioned on p. 362). A compound closely related to this has the formula $(NaPO_3)_6$, or $Na_6P_6O_{18}$. Its name is long but obviously quite suitable—sodium hexametaphosphate—and it is manufactured from phosphorus (via phosphoric acid) in very large quantities; but we need not go into the method used.

Now if we add a suitable quantity of this salt (in solution) to hard water, there is no precipitate. Perhaps we think, 'Then the calcium compound is still there, and the water will still be hard.' But it is not. It very readily gives a lather with soap. It is soft!

What has happened? Just this, that if we regard the sodium hexametaphosphate molecule as being made up of a 'metal' part (sodium) and an 'acid' part (hexametaphosphate), the calcium has entered the *acid* part. So placed, it no longer behaves like calcium, and the water is no longer hard. Because water softened in this way (unlike water softened by sodium carbonate) is free from precipitate, the laundryman much prefers it. It simplifies his rinsing problems, for instance. Thus sodium hexametaphosphate has become very popular for use both by itself, and as an ingredient of washing powders and various 'detergents'. It is used too for softening the water fed into boilers, and is often sold under the trade name of 'Calgon.'

Looking once more at the three formulæ

$$Na_3PO_4, \qquad Na_2HPO_4, \qquad NaH_2PO_4$$

let us consider what would be the formulæ of the corresponding *calcium* compounds. As calcium is divalent, we should have only one atom of calcium for every two of sodium, so that 'mathematically' the formulæ would be $Ca_{1\frac{1}{2}}PO_4$, $CaHPO_4$, $Ca_{\frac{1}{2}}H_2PO_4$.

Getting rid of fractions we have for the formulæ

$Ca_3(PO_4)_2$—tricalcium phosphate,
$CaHPO_4$—dicalcium phosphate,
$CaH_4(PO_4)_2$—monocalcium phosphate.

We look rather suspiciously at the name 'dicalcium,' but for fair comparison with the other names we must consider the number of calcium atoms combined with *two* PO_4 groups, and that of course would be two, 'mathematically' $Ca_2H_2(PO_4)_2$. One use of this dicalcium compound is as a mineral feed supplement for livestock. The mono- compound, like the corresponding sodium salt, is largely used as the 'acid' constituent of baking powder, but it is used in far greater quantities as a fertilizer, as we shall see in a moment.

We have already noticed the *tri*-compound in connection with 'rock phosphate.' Very finely ground, this is sometimes used as a fertilizer, but farmers generally find it too slow in action (because it is so very slightly soluble). When treated with sulphuric acid, however, it gives a mixture of monocalcium phosphate and calcium sulphate—a mixture known as 'superphosphate of lime,' or simply 'superphosphate,' the equation being

$$Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4$$

The monocalcium phosphate is much more soluble than rock phosphate, and so 'superphosphate' has come to be widely used as a quick-acting phosphate fertilizer.

Notice (from the last equation) that of the three calcium atoms in $Ca_3(PO_4)_2$, only one becomes useful phosphate. The other two become sulphate, which is not of much use to the farmer, and adds to the cost of carriage. Would it be possible to obtain a fertilizer which is *all* monophosphate?

This question received special attention in America, where because of the great distances involved, the question of carriage looms larger. The problem was solved by first preparing phosphorus, as described on p. 357, and then burning it to form the pentoxide, P_2O_5. This is treated with water at a suitable temperature to make orthophosphoric acid [$P_2O_5 + 3H_2O = 2H_3(PO_4)_2$], and the phosphate rock is then treated with this acid *instead of with* sulphuric acid.

$$Ca_3(PO_4)_2 + 4H_3PO_4 = 3CaH_4(PO_4)_2$$

The product is about three times as rich in phosphorus as the old mixture, and in fact is often sold under the name of 'triple superphosphate' or 'concentrated superphosphate.'

Chlorides of Phosphorus. If phosphorus (red or yellow) is placed in a deflagrating spoon and plunged into a jar of chlorine, it takes fire of itself, forming a mixture of phosphorus trichloride and phosphorus pentachloride:—

$$[P + 3Cl = PCl_3] \qquad 2P + 3Cl_2 = 2PCl_3$$

Similarly $$2P + 5Cl_2 = 2PCl_5$$

To prepare a quantity of the trichloride, phosphorus in small pieces is placed in a retort from which the air has been displaced by carbon dioxide. A stream of dry chlorine is then led over the phosphorus. The heat of the reaction causes the trichloride to distil over into a receiver, which is carefully protected from contact with atmospheric moisture. The product may be allowed to stand for a few hours over yellow phosphorus (to remove excess chlorine) and is then distilled.

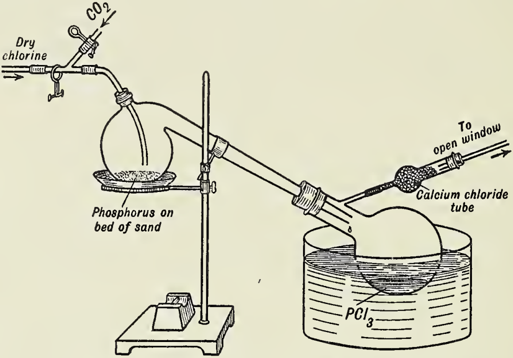

FIG. 31/4. Preparation of phosphorus trichloride

If instead of the yellow phosphorus we use an equal weight of the red variety, the yield of trichloride is just the same—further evidence of the identity of the two forms.

Phosphorus trichloride is a colourless liquid boiling at 76° C. It reacts rather violently with water, forming phosphorous acid, H_3PO_3:—

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$

It is because of this reaction that atmospheric moisture must be so carefully excluded when the trichloride is being prepared.

(*N.B.* Phosphor*ous* acid, H_3PO_3, because it contains one atom of oxygen less than phosphor*ic* acid, H_3PO_4. Cf. sulphur*ous* acid, H_2SO_3, sulphur*ic*, H_2SO_4; nitr*ous* acid, HNO_2, nitr*ic*, HNO_3, etc.)

Phosphorus pentachloride, PCl_5, is a pale yellow solid produced when the trichloride is allowed to drip into chlorine.

Like the trichloride, it reacts vigorously with water, phosphor*ic* acid being produced in this case

$$PCl_5 + 4H_2O = 5HCl + H_3PO_4$$

The chemical changes just considered (i.e. the action of water on phosphorus tri- and penta-chloride) are of a rather special type known as ***hydrolysis.*** We shall not be far wrong if we regard this as a double decomposition between two substances, one of which is water, and which results in the formation of two new substances, one of which is an acid.

In the case just considered *both* the new substances are acids, but this is rather unusual.

It is important to notice that an element whose chloride is readily hydrolysed by water is usually a *non-metal.* The chloride of a metal—sodium chloride, for instance—is not readily hydrolysed.

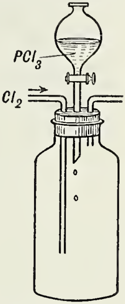

Fig. 31/5
Preparation of phosphorus pentachloride

Phosphine. Phosphorus forms several compounds with hydrogen, and we shall give some account of one of these. Its formula is PH_3, and it is known as phosphine, phosphorus trihydride or phosphoretted hydrogen.

To prepare it, about 10 gm. of yellow phosphorus, well covered with a strong solution of caustic soda, is placed in a flask arranged as in fig. 31/6. Air is displaced from the flask by means of coal-gas, and then the caustic soda is heated. Gas soon begins to be evolved, and as each bubble reaches the air it burns with a bright yellow flame, producing a vortex ring of smoke, which consists of phosphorus pentoxide. The main reaction taking place in the flask is represented by the equation

$$4P + 3NaOH + 3H_2O = 3NaH_2PO_2 + PH_3$$

(*N.B.* NaH_2PO_2 stands for sodium di-hydrogen hypophosphite. We have already had phosphor*ic* acid, H_3PO_4, giving rise to the phosph*ates*, and phosphor*ous* acid, H_3PO_3, giving rise to the phosph*ites*; with still less oxygen we have H_3PO_2, hypophosphorous acid, giving rise to the hypophosphites.)

The equation representing the burning of phosphine is

$$2PH_3 + 4O_2 = P_2O_5 + 3H_2O$$

Although phosphine takes fire at quite a low temperature (100° C. or so), it is not really spontaneously inflammable. It has been shown that this property is due to the presence of small quantities of a liquid hydride having the formula P_2H_4. If the gas obtained from caustic soda and phosphorus is passed through a U-tube containing a freezing mixture, it ceases to be spontaneously inflammable—the liquid hydride having been removed by condensation.

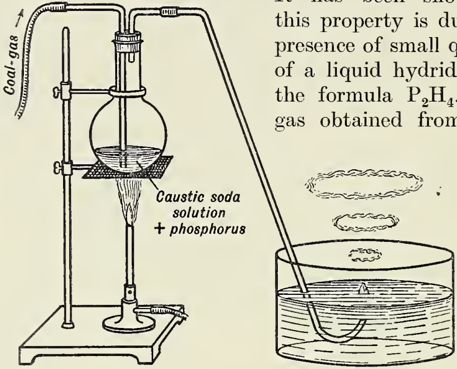

FIG. 31/6. Preparation of phosphine

Phosphine possesses a strong smell rather suggestive of garlic.[1] It is very poisonous. Its formula, PH_3, reminds one of ammonia, NH_3, and just as ammonia will give rise to ammonium chloride, so (at low temperatures) phosphine will give rise to phosphonium chloride.

$$NH_3 + HCl = NH_4Cl$$
$$PH_3 + HCl = PH_4Cl$$

Unlike ammonia, however, phosphine is only slightly soluble in water, and its solution is not alkaline to litmus.

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[1] The smell noticed when water is poured on to calcium carbide, and usually attributed to acetylene, is chiefly due to the presence of traces of this gas. It is produced by the action of water on calcium phosphide, minute traces of which are present in the carbide.

Matches. Matches in something like their modern form were invented about the year 1832. The head consisted of yellow phosphorus, mixed with an oxidising agent such as potassium chlorate, $KClO_3$, red lead, Pb_3O_4, manganese dioxide, MnO_2, etc. The mixture contained a little gum to hold it together. On rubbing the match against sand-paper, the friction raised the temperature sufficiently to start a chemical action. This consisted of rapid oxidation of the phosphorus, in the first place by the oxygen obtained from the potassium chlorate, etc., and then by the oxygen of the air. The oxidation was so vigorous as to be accompanied by flame.

As already mentioned, however, yellow phosphorus is a deadly poison, and since 1912 the manufacture of matches containing yellow phosphorus has been prohibited, practically throughout the world. The strike-anywhere match of to-day contains not phosphorus, but a *sulphide* of phosphorus, P_4S_3, mixed with an oxidising agent as before. Since the phosphorus is oxidised to pentoxide and the sulphur to dioxide, we can easily calculate that 16 atoms of oxygen will be required (10 for the phosphorus and 6 for the sulphur), so we may write the equation:—

$$P_4S_3 + 8O_2 = 2P_2O_5 + 3SO_2$$

The safety match, intended to strike only on a prepared surface, was invented as long ago as 1844. The head of the match contains various oxidising agents (e.g. potassium chlorate and red lead) mixed with antimony sulphide, Sb_2S_3. The essential constituent of the prepared surface is red phosphorus. When the match head rubs against this, a little of the phosphorus is at once oxidised by the oxygen contained in the potassium chlorate,[1] red lead, etc. The heat thus produced is sufficient to start the main chemical action, which takes place in the match itself between the antimony sulphide and the various oxidising agents.

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[1] Many a burnt pocket has resulted from this reaction. A man has bought 'throat lozenges' consisting of potassium chlorate, and one or two of these have escaped from the packet and rubbed against the surface of his match-box. With one of these lozenges and a (safety) match-box it is easy to light a bunsen burner.

$$[Sb_2S_3 + 9O = Sb_2O_3 + 3SO_2]$$
$$2Sb_2S_3 + 9O_2 = 2Sb_2O_3 + 6SO_2$$

A good match should soon cease to glow when blown out (otherwise there is some risk of fire being caused). To secure this, the splints, before receiving their heads, are boiled for two hours in a solution of borax, a substance which on heating gives off its water of crystallisation as steam, and then melts to a sort of glass. You can no doubt think out for yourself how the presence of such a substance would help to prevent glowing.

Questions

N.B. *See note in italics*, p. 132

1. Describe the manufacture of phosphorus from calcium phosphate. How can red phosphorus (*a*) be obtained from, (*b*) be converted into, white phosphorus? *O.C.*

2. Compare and contrast the two common forms (allotropes) of phosphorus.

Starting with phosphorus, describe how you would prepare specimens of (*a*) phosphoric oxide, and (*b*) phosphoric acid.

Give the formula of the mineral in which phosphorus occurs most abundantly. *Dur.*

3. If there were no waste, how much calcium phosphate, $Ca_3(PO_4)_2$, would be needed to furnish 1 ton of phosphorus?

4. A substance has the following percentage composition: sodium 21·7, hydrogen 1·9, phosphorus 29·2, oxygen 30·2, water of hydration 17·0. What is its simplest formula? What is it called, and how do you think it might be prepared?

5. Give some account of the phosphorus compounds used *either* as fertilizers *or* as water softeners.

6. What is the action of water on phosphorus trichloride? *Lond.* (*part*)

7. Explain the chemical changes that take place when one strikes *either* a 'strike anywhere' match *or* a safety match.

CHAPTER 32

CHEMISTRY AND THE SOIL

Origin of the Soil. A study of the soil is evidently the concern of other sciences besides chemistry—of physics, geology and botany, for instance. In this brief account therefore, though we shall emphasise the chemical side of the question, we shall certainly not be able to limit ourselves to it.

The soil has its origin in the *rocks*—those masses of naturally occurring solid substances of which the earth's crust is composed. Granite and sandstone, for instance, are rocks, though they have been formed by very different processes.

In various ways the upper part of the rock surface becomes broken up. It is cracked by rather rapid changes of temperature, as when a cold night follows a hot day. It is also cracked when water soaks into it and afterwards freezes, owing to the fact that, in freezing, water expands. Chemical processes may play a part, as when a rock containing some iron compound is oxidised by the air. This causes ferric oxide (Fe_2O_3) to be formed, a reddish-brown substance which easily breaks away from the main bulk.

In these and other ways the rock is broken into small fragments, and soil is gradually formed. Sometimes it is carried away from the place in which it was originally produced. We can see this happening, for instance, when a river is coloured brown by the particles it is carrying. Sooner or later (usually at the river mouth) the particles are deposited as 'silt' or 'alluvium,' and so an alluvial deposit is an example of a 'transported' soil. Most soils, however, have a composition broadly similar to that of the rocks over which they lie. Between the soil and the underlying rock is the *sub-soil.* This differs considerably from soil, partly because it has not been subject so much to the action of the air, but chiefly because it contains little or no *humus.* Humus is a dark-brown substance formed by the decay of vegetation—in concentrated form we meet with it as peat.

Composition. Besides humus, the ordinary constituents of soil are sand, clay and chalk. Pure sand is silica, SiO_2, but it is nearly always associated with the oxide of iron of which we have spoken. Pure clay is kaolin or china clay (aluminium silicate). Actually this is seldom present to the extent of more than 1 or 2 per cent., and the term 'clay' simply means a substance in which sand, felspar, etc., are present in a very fine state of sub-division, with a small proportion of aluminium silicate. It is the very small size of the particles which gives it the peculiar property of being sticky when wet, and of setting to a hard, brick-like mass when dry.

Pure chalk, of course, is calcium carbonate, $CaCO_3$, but magnesium carbonate and calcium phosphate are often present along with it.

Soils are distinguished according to the relative proportions of these four main constituents, sand, clay, chalk and humus. Thus a *loam* is a mixture in which clay and sand predominate. With from 70 to 85 per cent. of sand it would be a 'sandy loam,' while with those percentages of clay it would be a 'clayey loam.' A mixture of clay and chalk (with little sand) would be a *marl* and so on.

It is easy to see how each of the above-mentioned four substances contributes to the qualities of a good soil. Thus sand contains no plant food, and allows water to flow through it very readily. Clay holds water all too well, but at the same time this water holds plant food in solution. Evidently a mixture of sand and clay is much better than either taken singly. Humus again, though very rich in plant food, tends to be 'sour,' owing to the presence of organic acids. These acids are neutralised by calcium carbonate (the corresponding calcium salts being formed). Further, calcium carbonate, and still more the related substance, slaked lime, has the property of making the very fine particles of clay coagulate to form larger particles. That is why a clay soil is more workable if chalk is also present. If a farmer finds that his soil is difficult to work because of excessive clay, or if it is 'sour,' he often gives it a dressing of lime.

Chalk plays another important part somewhat related to its correction of sourness. By a series of changes which we shall consider later in the chapter, atmospheric nitrogen is converted into nitric acid, which enters the soil. This is at once neutralised by chalk (or by added lime), forming calcium nitrate, which can be used by the plants.

Air and Water Necessary. Besides the solid constituents of which we have spoken, a soil must also contain air and water if it is to be of use to plants. They are, of course, present in the spaces between the soil particles. Even in an apparently 'dry' soil, these particles are usually surrounded by a film of moisture.

Air in soil is needed to enable seeds to germinate and roots to breathe. Further, as we shall see presently, the nitrogen of this 'soil air' may in certain circumstances be turned into nitrogen compounds which plants can use as food.

Speaking generally, the oxygen present in soil air is used up in processes of oxidation. Hence soil air contains less oxygen but more carbon dioxide than ordinary air.

Notice that soil air and atmospheric air are constantly mixing (though perhaps not very rapidly). When soil becomes heated, the contained air expands and some of it escapes into the atmosphere. When it cools, atmospheric air is drawn in. Increase of atmospheric pressure also drives more air into the soil, while with a lowering of pressure some of the soil air escapes. Quite apart from these changes of temperature and pressure, soil air and atmospheric air are constantly mixing by the process of *diffusion* (p. 136)—the same process which causes a little escaping coal-gas, in time, to become evenly mixed with the air of a room.

Fertilizers. The various compounds in the soil are formed from a total of about twenty elements. For most of these the supply never seems to run short, however many crops are grown. No doubt the soil obtains fresh supplies from the sub-soil (and the sub-soil in turn from the underlying rock) at a sufficient rate to balance what is taken by the plants.

In three cases, however (besides that of lime, which has already been discussed), this happy state of balance is not maintained. We refer to compounds of (1) nitrogen, (2) potassium and (3) phosphorus. In some cases there would be no shortage of (2) or (3), while in others there might be a deficiency of some other substances, such as compounds of magnesium. Still, in general we may fix our attention on the three mentioned. For successful cropping, suitable compounds of nitrogen, potassium and phosphorus have to be added, preferably as farm-yard manure, but failing that as 'artificial' fertilizers.

In more primitive times, when people with their sheep and cattle lived on a self-contained farm, this problem of artificial fertilizers did not arise. Everything taken from the soil was returned to it, chiefly in the form of manure. The modern situation is well illustrated, say, by a farm in Manitoba, from which many tons of wheat may be raised every year and sent far away.

The Nitrogen Cycle. We will deal first with the case of nitrogen. As already mentioned, the plant can make no direct use of the free nitrogen present in the air. It needs its nitrogen in the form of *nitrates*. Under natural conditions these are produced in two ways.

(*a*) As a result of electric discharges in the atmosphere (e.g. lightning flashes) nitrogen and oxygen combine, forming nitric oxide, NO. This is quickly oxidised to the dioxide, NO_2, which then by the action of moisture is converted into nitric and nitrous acids (equations on p. 352). This extremely dilute nitric acid descends as rain, and is neutralised by some such substance as chalk in the soil to form, say, calcium nitrate.

$$CaCO_3 + 2HNO_3 = Ca(NO_3)_2 + H_2O + CO_2$$

(*b*) By the action of certain bacteria. These obtain their food from the roots of various leguminous plants such as beans, peas, clover, etc., to which they attach themselves. In return, they convert the free nitrogen present in the soil-air into the nitrates needed by the plant—they 'pay for their board' so to speak. Such a partnership is known as *symbiosis* (*Gk. syn*=together, *bios*=life). If you dig up the root of a broad bean you will see whitish nodules, perhaps $\frac{1}{8}$ inch in diameter, attached to the root. These are colonies of the bacteria in question.

The nitrates taken up by the plants undergo a complete round of changes known as the *nitrogen cycle*. First, the plant turns them into very complex compounds known as plant proteins. When the plant dies it decays—a process which includes the breaking down of its proteins into ammonia by bacteria. If the plant is eaten by an animal the plant proteins are converted into animal proteins, and we still get ammonia, either from the waste products of the animal or when it dies from the decay of its body.

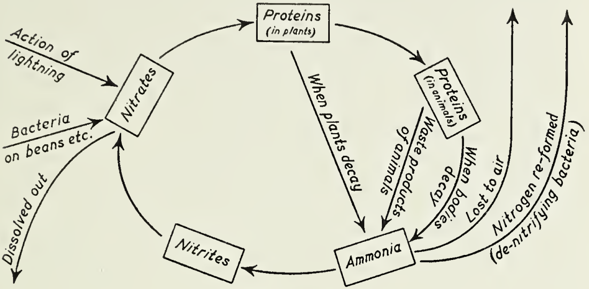

FIG. 32/1

Other bacteria seize upon the ammonia, and in the presence of soil-air and some acid-neutraliser, such as chalk or lime, turn it into nitrites. Still others turn the nitrites into nitrates—and the cycle is complete.

As we should expect, there are certain leakages in the course of the cycle. To begin with, nitrates are very *soluble* substances, and some will be washed out by the rain. Again, at the 'ammonia' stage, some of the gas is sure to be lost to the air (as an extreme case we have the manure heap, where we can smell it). At this stage too, we have to contend with 'denitrifying bacteria,' which turn the 'fixed' nitrogen back into the free element.

However, under natural conditions these losses are made good by the processes already mentioned (action of lightning, and of bacteria attached to the roots of leguminous plants).

'But aren't there rather a *lot* of bacteria?' you ask. There certainly are. It is calculated that 1 cub. centimetre of surface soil contains from 1½ to 2 millions of them. They are highly specialised too. Dr. Slosson, in his *Creative Chemistry*, compares them with strict trade-unionist bodies, 'The Amalgamated Union of Nitrate Workers' and so on. They will do their own particular job and no other. However, taken as a whole, the various groups must be very efficient, for they turn as much as 96 per cent. of the ammonia into nitrates. We may summarise the round of changes somewhat as shown in fig. 32/1, where also the various 'leakages' are indicated, and the means by which these are made good.

This conversion of ammonia into nitrates is, of course, a process of oxidation, and we may compare it with the process by which nitric acid is *manufactured* from ammonia (p. 353). In that case, platinum was used as the catalyst. There may be some substance in the soil (or in the bodies of the bacteria) having a catalytic action, but if so, it is certainly not platinum.

As already indicated, while the supply of combined nitrogen in the soil is maintained under 'natural' conditions, it soon becomes depleted if crops are regularly grown and sent away. The deficiency has to be made good by supplying nitrogen fertilizers. Until the early 1900s these consisted of sodium nitrate from the Chile deposits, supplemented by a somewhat smaller amount of ammonium sulphate from the gas-works. As already mentioned, however (p. 2), Sir William Crookes in 1898 showed that such supplies were not sufficient to meet future needs, and that before many decades the world would be faced with famine, unless some means could be found of 'fixing' the inexhaustible supplies of free nitrogen in the atmosphere.

Within seven years the problem was solved by the 'arc' process of Birkeland and Eyde, but this has long since been superseded by the Haber–Bosch synthetic ammonia process (p. 325). From ammonia it is easy to prepare a whole range of nitrogen fertilizers, beginning with ammonium sulphate. We have seen how the ammonia can be catalytically oxidised to nitric acid, from which nitrates are easily made—including the sodium nitrate for which we formerly depended on Chile! Ammonium nitrate, NH_4NO_3, would obviously be a particularly rich fertilizer, because it contains nitrogen in both parts of the molecule. It would, however, be rather difficult to use by itself because it is *hygroscopic* (i.e. it takes up moisture from the air), but mixed with limestone it is quite manageable in this respect, and has a wide sale under the name 'nitrochalk.'

Another valuable nitrogen fertilizer, urea, $CO(NH_2)_2$, is likewise easily made from ammonia, and is coming into increasing use. It contains 47·1 per cent. of nitrogen, and so is an even more concentrated fertilizer than ammonium nitrate (35 per cent.). In the soil it is rapidly converted into ammonia.

As might be expected, nitrogen fertilizers are manufactured on an enormous scale. In Great Britain alone, during the year 1955, 1,010,000 tons of ammonium sulphate were manufactured (besides other ammonium salts, and urea). It is rather difficult to imagine such a quantity, but if it were loaded into railway trucks, 10 tons to each truck, the line would stretch for about 330 miles, and when the engine was passing through London the guard's van would be well to the north of Newcastle!

Leaving now the subject of nitrogenous fertilizers, we turn to potash. The name is derived from *pot ashes*—the ash obtained by burning wood and garden refuse in iron pots, and which contains perhaps 6 per cent. or so of potassium carbonate,[1] K_2CO_3. Every gardener knows that the ashes of his garden bonfire are good for the ground (the writer knows of one or two who give every encouragement to Fifth of November bonfires in their immediate neighbourhood). If as often happens, the amount of ash he can obtain is insufficient, he buys a certain amount of potassium sulphate, K_2SO_4, or chloride, KCl ('muriate of potash'). There are large supplies of potassium salts at Stassfurt in Germany and a few other parts of the world, and we import what we need. There are large deposits in the Whitby district of Yorkshire, but they are at a great depth—about 4,000 feet—and mixed with other substances from which separation is difficult. So far at any rate, the efforts made have resulted in failure.[1]

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[1] The extraction of potassium carbonate from wood ash is described on p. 199 of the author's *School Course of Practical Chemistry* (Bell).

Finally, we must consider phosphates. As mentioned in our last chapter, calcium phosphate, $Ca_3(PO_4)_2$, forms the chief constituent of bone, and it has long been known that land benefits from an occasional dressing of ground bone. This, however, is only *very* slightly soluble, even in the presence of carbon dioxide (giving carbonic acid), and so the farmer had to wait a long time for results.

About the year 1837, however, John Bennet Lawes turned his attention to the matter. He was a comparatively well-to-do landowner living on his farm at Rothamsted, Harpenden (Herts), and had had a good education at Oxford, taking a special interest in chemistry. In the year mentioned he was twenty-two.

He knew that the difficulty about bones was their insolubility, and soon found that by treatment with sulphuric acid they could be turned into the much more soluble 'superphosphate,' $Ca(H_2PO_4)_2$ (p. 365). An actual trial on his farm gave him the result he expected and hoped for—that the superphosphate was effective far more quickly than the untreated bone. He thought of large-scale operations, but alas! the supply of bones to be obtained was far too meagre.

Then he thought of 'rock phosphate' (p. 357), derived apparently from the fossilised remains of pre-historic animals. It occurs abundantly in various parts of the world, and proved to be just the material he needed. In a barn at Rothamsted he made a few hundredweights of superphosphate by way of experiment, and in 1842 he patented his process.[2] It turned out to be enormously successful, and in 1872 he sold out his manufacturing interests for £300,000!

It is interesting to notice that while in 1850 about 5,000 tons of rock phosphate were turned into superphosphate, in 1950 the world output had grown to over 20 million tons.

We may add that Lawes, working with another chemist,

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[1] After work extending over several years and involving the expenditure of £400,000, Imperial Chemical Industries Ltd. decided in 1954 to cut its losses.

[2] Some account of a modern process by which a much improved product ('triple phosphate') may be obtained, has been given on p. 365.

J. H. Gilbert, continued his experiments in scientific farming to the end of his long life (he died in 1900, in his eighty-sixth year). He left his farm and £100,000 in money to be administered by a Trust in the interests of the nation, and the old farm at Rothamsted is to-day one of the world's most famous centres of agricultural research.

Questions

1. Explain how each of the constituents humus, sand, clay and chalk contribute to the qualities of a good soil.

2. What differences would you expect to find between the composition of ordinary air and that of the air entangled in soil. Give reasons.

3. Land which is constantly being cropped is likely to become short of certain substances. What are these? Explain how the chemist has helped in providing them.

4. What do you understand by the Nitrogen Cycle?

5. Give some account of the action of soil bacteria.

6. What objection if any do you see to (i) adding lime to garden soil at the same time as superphosphate; (ii) adding lime at the same time as ammonium sulphate; (iii) adding sodium nitrate in the autumn?

CHAPTER 33

SILICA

Occurrence. Of a few miles of the earth's crust which men have been able to examine, silicon is the most abundant constituent with the exception of oxygen, being present to the extent of about 26 per cent. It is never found in the free condition, but its oxide silica, SiO_2, is extremely abundant.

This oxide is found in several crystalline forms, the most important being quartz, or rock-crystal. Crystals of this, consisting of hexagonal prisms surmounted by pyramids,[1] are often met with. Sometimes they are very large—occasionally as much as a yard or more in length—and one has been known to weigh nearly a ton.

Crystals of quartz
By permission of the British Museum (Natural History)

Sand consists of small grains of quartz mixed with one or more other substances, the commonest being oxide of iron. In sandstone these are pressed together, the soft iron oxide acting as a sort of cement to bind together the harder particles of quartz.

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[1] These crystals greatly interested the ancients. The Greeks thought they consisted of ice frozen so hard by the intense cold of the Alps that it was impossible to melt them. Hence they called the crystals *krystallos* (clear ice), a name which was later extended to include all crystalline substances.

So far we have spoken only of crystalline silica, but amorphous forms of this oxide are also found. *Kieselguhr*, for instance, consisting of the skeletons of tiny organisms known as diatoms, is almost pure amorphous silica. It is very porous and will actually absorb three times its own weight of the explosive liquid nitro-glycerin. The product is dynamite.[1]

Flint is chiefly amorphous silica, but contains a little quartz.

Agate is a somewhat similar mixture. On account of its hardness it is used for making the 'knife-edges' of balances.

Mortars and pestles that are to be used for grinding very hard substances are also sometimes made of agate.

Uses. Some of these have already been mentioned. We may add that it is possible to make very large lenses of clear quartz, and as these do not crack with sudden heating (silica having a very low coefficient of expansion), they are excellent for use in cinema lanterns.

At a very high temperature silica can be softened like glass, and it can then be shaped into crucibles, flasks, etc. A remarkable property of such apparatus is that, for the reason just given, it can be made red-hot and then suddenly cooled in water without cracking. Silica dishes, etc., of attractive appearance are now being made for domestic use.

Quartz is also used for making the very thin filaments by which small magnets, etc., are suspended in delicate electrical instruments. The method of manufacture is curious, an arrow and small cross-bow being employed. The arrow consists of a stiff straw about 6 inches long, weighted with a needle along the forward part to give it stability in its flight. A short length of thin wood is fitted into the 'tail' end.

A thin pencil of quartz, AB, is drawn out so that the drawn-out portion BC is only about $\frac{1}{50}$ inch in diameter, and the end C is fastened with sealing wax to the wooden tail of the arrow. A very fine oxy-hydrogen blowpipe flame is then directed on a point between B and C so as to produce local melting of the quartz, and the arrow is then shot a distance of 30 feet or so. A thread of quartz is drawn behind it, so thin that it hardens immediately. It is found that the threads are wonderfully uniform in thickness and have a tensile strength equal to that of the very best steel. They can be made much finer than any spider's web, and untwist almost perfectly after being subjected to torsion.

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[1] Such dynamite contains, however, at least 25 per cent. of the inert kieselguhr, which diminishes its explosive force. For this reason the present tendency is to use, as absorbent, more 'active' materials such as wood flour, sodium nitrate or ammonium nitrate — especially the last.

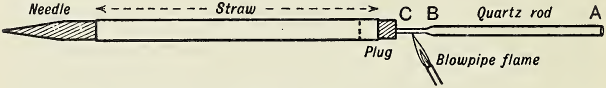

FIG. 33/1. Making a quartz filament

By far the most important use of silica, however, consists in the manufacture of glass, and we must now consider the chemical principles underlying this process.

Silica an Acidic Oxide. We must first understand that silica is an *acid-forming oxide.* Such oxides usually combine with water to form an acid (e.g. sulphur trioxide forms sulphuric acid). Silica does not do this—nothing happens, for instance, when sand is stirred up with water. But silicic acid may be obtained by other means, as we shall see presently, and when this acid is heated, silica is produced. In short, though it is *not* true that silica + water = silicic acid, it *is* true that silicic acid = silica + water.

Further, it is characteristic of an acidic oxide that it will combine with a basic oxide, forming a salt, e.g.

$$CO_2 \text{ (acidic oxide)} + CaO \text{ (basic)} = CaCO_3$$

Now silica does combine with basic oxides, forming salts known as silicates, showing once again that it is an acidic oxide.

Sodium Silicate. Glass. Thus, if silica is fused with sodium oxide, sodium silicate is produced:—

$$Na_2O + SiO_2 = Na_2SiO_3$$

In practice, sodium *carbonate* is employed, the mixture being heated in a furnace.

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$$

The product is dissolved in water under pressure, and the familiar *water-glass* is thus obtained. It is much used for preserving eggs, its action depending on the fact that it seals up the pores of the shell and keeps air from entering. It is largely employed as a gum in the cardboard-box industry, and it has many other uses.

If silica is fused with a mixture of sodium carbonate and calcium carbonate, a mixture of sodium and calcium silicates is produced.

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$$
$$CaCO_3 + SiO_2 = CaSiO_3 + CO_2$$

This substance is the ordinary 'soda glass' so much used in the laboratory. Window glass is similar, but it contains a larger amount of silica, which causes it to have a rather higher melting-point. Its composition is expressed roughly by the formula, $Na_2SiO_3 \cdot CaSiO_3 \cdot 4SiO_2$.

'Hard glass,' used in the laboratory for combustion tubes, etc., is made by using *potassium* carbonate instead of sodium carbonate, so that hard glass is a mixture, or compound, of potassium and calcium silicates.

Many other kinds of glass are known.[1] Thus it is desirable that 'cut glass' should be as dense as possible, so that it may have a high index of refraction (which makes it sparkle). The high density is secured by arranging that one of the substances present shall be *lead* silicate (the other one being sodium or potassium silicate). Such a glass is made by fusing silica with sodium (or potassium) carbonate and red lead (Pb_3O_4). The formation of lead silicate would be represented by the equation

$$[Pb_3O_4 + 3SiO_2 = 3PbSiO_3 + O]$$
$$2Pb_3O_4 + 6SiO_2 = 6PbSiO_3 + O_2$$

You may have noticed that one result of heating an oxide of lead in a test-tube is that the test-tube always cracks. The lead oxide combines with silica present in the glass, forming lead silicate, and the cracking is due to the fact that this silicate does not contract by the same amount as the rest of the glass. The green colour often seen in cheap bottle glass is due to the presence of silicate of *iron*. Remembering that sand usually contains oxide of iron, you can easily see how this particular silicate finds its way into the glass. *Glazing* consists in the depositing of a thin film of glass over a surface, usually with the object of making it non-porous. For an obvious reason, this film should expand at the same rate as the material which it covers. You can illustrate the process of glazing by taking a little silica, litharge (PbO) and anhydrous sodium carbonate and mixing into a cream with water. A bit of plant pot covered with this and baked in a muffle furnace, or in the middle of a good fire, is soon glazed.

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[1] Some of the modern glasses often contain other acidic oxides, e.g. 'Pyrex' glass contains borates rather than silicates.

Cheap goods, such as earthenware drain-pipes, are *salt-glazed*. Salt is thrown into the kiln, vaporises at the high temperature, and in the presence of water vapour reacts with the silica present in the clay. A glaze of sodium silicate is produced and hydrogen chloride is given off:—

$$2NaCl + H_2O + SiO_2 = Na_2SiO_3 + 2HCl$$

The subject of glass manufacture is evidently a very wide one, but one simple chemical principle runs through it all. This is that silica, an acidic oxide, will combine with various basic oxides, forming salts known as silicates; glass being a mixture (or perhaps a complex compound) of two or more of these silicates.

By courtesy of 'Oil-Power'

An ancient Egyptian industry

Glass-making and glass-blowing are very ancient industries, as is proved by the fact that coloured glass beads have often been found interred with Egyptian mummies. The illustration apparently represents two of these primitive glass-blowers. It is taken from an Egyptian tomb-painting of date about 2000 B.C., but opinion is divided as to whether the industry represented is glass-blowing or a primitive method of copper smelting.

Of late years there have been great advances made in the manufacture of glass, and perhaps some day we shall see really unbreakable glass. Already one firm advertises a flask with which it is possible to drive a $1\frac{1}{2}$ inch nail up to the head into soft wood!

Clay. A very pure clay, known as *china-clay* or *kaolinite*, consists of a hydrated silicate of alumina with the formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. It is the chief constituent of *porcelain*.

An impure clay is used for making *bricks*, the red colour being due to the presence of ferric oxide, Fe_2O_3.

For making *earthenware*, a clay of intermediate purity is employed.

Before being 'fired,' wet clay is very plastic and can be moulded to any desired shape—an essential property for the making of pottery. After firing, the '$2H_2O$' of the formula is permanently lost, and the product can no longer be rendered plastic. It is now porous, and for most purposes has to be glazed by one of the methods already described.

Cement. This is made by heating a mixture of limestone and clay in a suitable kiln till it just begins to fuse. The product is cooled forming a 'clinker,' and when this is finely ground (so finely that it would pass through a sieve which would hold water), we have *Portland cement*.

Its composition is very complex, but the substances chiefly concerned in 'setting' appear to be tricalcium silicate, $(CaO)_3 \cdot SiO_2$, and tricalcium aluminate, $(CaO)_3 \cdot Al_2O_3$. When water is added, the former is not affected, but the latter is converted into a mixture of calcium and aluminium hydroxides, $Ca(OH)_2$ and $Al(OH)_3$. The calcium hydroxide gradually crystallises out, the crystals serving to bind together the fine particles of tricalcium silicate. The pores of the structure thus formed are filled with the aluminium hydroxide, with the result that a highly impervious mass is produced.

Large quantities of cement are made in Great Britain in connection with the manufacture of sulphuric acid (p. 290). The substances required are anhydrite $CaSO_4$, sand (to provide silica, SiO_2), coke and suitable furnace ashes (containing alumina, Al_2O_3, and ferric oxide, Fe_2O_3). These are mixed in the correct proportions and strongly heated in immense rotary kilns.

The anhydrite is reduced by the coke to calcium sulphide, which then reacts with more anhydrite forming calcium oxide and sulphur dioxide:—

$$CaSO_4 + 2C = 2CO_2 + CaS \quad . \quad . \quad (i)$$

$$CaS + 3CaSO_4 = 4CaO + 4SO_2 \quad . \quad . \quad (ii)$$

The sulphur dioxide is used for making sulphuric acid, while the quicklime reacts with silica, forming tricalcium silicate, $(CaO)_3 \cdot SiO_2$ and tricalcium aluminate, $(CaO)_3 \cdot Al_2O_3$. The mixture provides the 'cement clinker.'

The reaction with water has already been discussed. The ferric oxide present, Fe_2O_3, probably behaves in a similar way to the alumina, Al_2O_3.

Silica from a Silicate. We have had many examples of the conversion of silica into silicates. We must now see how we can carry out the reverse process.

If we pour hydrochloric acid into a strong solution of water-glass, a white precipitate is obtained. This precipitate is often described as silicic acid, $H_2SiO_3(=H_2O \cdot SiO_2)$,[1] the equation being written

$$Na_2SiO_3 + 2HCl = 2NaCl + H_2SiO_3$$

The precipitate may be washed by decantation, dried and heated, when a fine white powder consisting of amorphous silica remains:—

$$H_2SiO_3 = H_2O + SiO_2$$

It is interesting to notice that we can obtain silicic acid in what is called a 'colloidal' form instead of as a precipitate. To obtain the colloidal acid, we have only to add a solution of water-glass to hydrochloric acid, instead of vice versa. In a few minutes the liquid sets to a stiff jelly. From this jelly, by rather special methods, the admixed sodium chloride, excess of hydrochloric acid and most of the water may be removed, and we then have *silica gel*. Because of its highly porous structure, this gel is sometimes used to provide a supporting framework for a catalyst (e.g. platinum in the 'Contact process' for sulphuric acid). It can also take up large quantities of water, and so is used as a drying agent for gases. The water is easily driven off by heating, and the gel can then be used again.

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[1] The composition of this precipitate varies with the conditions, and it is perhaps safer to use the less precise formula $SiO_2 \cdot xH_2O$.

Glass a Supercooled Liquid. 'Hypo' has a melting-point of 48° C., but if molten hypo is allowed to cool down without disturbance, it may easily reach room temperature, 15° C. or so, without solidifying.

On shaking, or especially on adding a small crystal of solid hypo, the liquid solidifies to a mass of crystals and the temperature at once rises to 48° C., the true melting-point.

The state of things just described is very common, though not many substances show it so clearly as hypo. The phenomenon is known as *supercooling*.

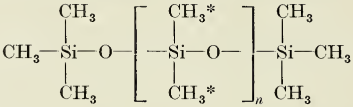
Glass is capable of supercooling to a very marked extent. As the molten glass cools it 'flows' less and less easily, like very cold honey or treacle, until finally it will not flow at all. It *looks* like a solid, but really it is just an extremely viscous liquid, corresponding to the supercooled hypo. Here, however, the likeness ends, for while it was easy to make the hypo become a true crystalline solid, we cannot easily induce a similar change in the glass. No doubt this is because the liquid offers so much resistance that the molecules are unable to take up the regular formation that is necessary for crystalline structure—just as a tightly-packed crowd of soldiers would be unable to 'form fours.'

If glass is kept near its melting-point for a long time the resistance to molecular movement is reduced, and the molecules may have time to arrange themselves in the necessary pattern. In that case the glass becomes a true crystalline solid—it is said to 'devitrify.' Devitrified glass is too brittle to be of any use.

We may notice that glass is by no means the only case of a supercooled liquid. Pitch and rubber are other examples, and so is plastic sulphur, which (as we have seen) becomes crystalline in the course of a few days.

Silicones. Although the compounds known as silicones have a somewhat complicated structure, they are becoming important in so many ways that we must say at least a little about them. Before reading what follows, it would be well to revise Chapter 19, and especially to notice why groups such as CH_3^- and $C_2H_5^-$ are univalent.

Silicon, like carbon, is tetravalent, and a structural formula which applies to a whole series of silicone fluids is

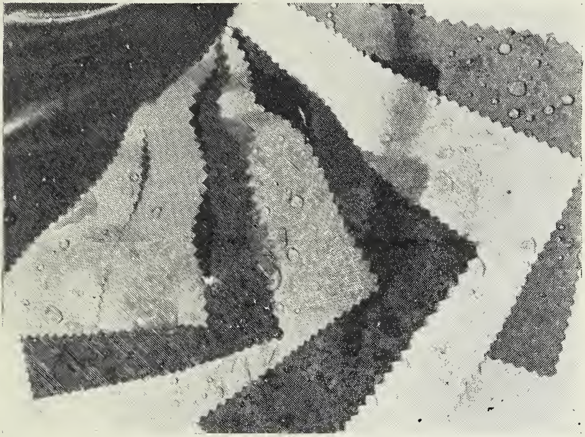


$$\mathrm{CH_3-}\underset{\substack{|\\ \mathrm{CH_3}}}{\overset{\substack{\mathrm{CH_3}\\ |}}{\mathrm{Si}}}\mathrm{-O-}\left[-\underset{\substack{|\\ \mathrm{CH_3^*}}}{\overset{\substack{\mathrm{CH_3^*}\\ |}}{\mathrm{Si}}}\mathrm{-O-}\right]_n-\underset{\substack{|\\ \mathrm{CH_3}}}{\overset{\substack{\mathrm{CH_3}\\ |}}{\mathrm{Si}}}\mathrm{-CH_3}$$

n can have many different values—in the case of silicone rubbers it runs into thousands! Again, instead of the CH_3^- group, we may have $C_2H_5^-$, $C_6H_5^-$ and many others. Further, while the formula given above is just a long chain, it is possible to oxidise such groups as those marked * in such a way as to replace CH_3^- by O^-. That gives us the characteristic $^-O^-$ Si $^-O^-$ formation starting off as a branch line, and by linking up with a chain of the original type, this branch line may become a very long one. One can see other possibilities, but enough has been said to show that the number of possible silicones is simply enormous. Even so, they have many properties in common. Thus the silicone fluids, often oily liquids, show only slight change of viscosity (i.e. 'thickness') with change of temperature, and so in the hottest summer a motorist could use the same grade of oil that served him in the depth of winter. They are not very easily oxidised, and so paint with a silicone admixture stands up very well to adverse weather conditions.

The silicone resins are much used as (electrical) insulators. If owing to a short-circuit there is gross overheating, oxidation results in the formation of silica—itself a very fair insulator. With ordinary insulation the corresponding product is, of course, carbon—a fair conductor—and the results may be disastrous.

To note just one more of a number of interesting properties, silicones are in general *water repellent*. For instance, on a glass surface treated with a silicone, the water, instead of forming a very thin continuous film (the cause of many failures in electrostatic experiments) runs together in isolated drops. This property is utilised in making cloth shower-proof, in waterproofing leather and in the treatment of brickwork.



By courtesy of Midland Silicones Ltd

Water-repellent property resulting from silicone treatment

Research still goes on, and the future certainly holds wonderful possibilities for the group of compounds we have so briefly discussed.

Questions

1. Give the formula of silica and name *two* naturally occurring forms of this substance.

Outline the method of manufacture of (*a*) water-glass, (*b*) common glass. Why is common bottle glass often green or brown in colour?

Given water-glass, how would you prepare a specimen of silica? Give equations. *Lond.*

2. (*a*) What would be the effect of heating a mixture of sand and sodium carbonate to bright redness, and what would be the properties of the substance produced?

(*b*) What would be the result if some lime was added to the mixture before heating?

(*c*) Give reasons for regarding silica as an acid-forming oxide.

(*d*) How would you separate salt from a mixture of sand and salt, and how would you prove that the salt was completely removed? *Dur.*

3. Makers of silica crucibles advise their customers not to heat strong alkalis (e.g. caustic soda) in them. Why?

4. How is cement made? What chemical processes are concerned in its setting?

CHAPTER 34

ELECTROCHEMICAL SERIES AND ELECTROLYSIS

Electrochemical Series. Fig. 34/1 represents a very simple form of voltaic cell. The current flows from copper to zinc *outside* the liquid, and therefore from zinc to copper *inside.* Zinc is said to be 'higher than copper' in the electrochemical series (sometimes called the electromotive series). Similarly, copper is higher than silver. Ignoring certain qualifications, we may say that it is possible to arrange the metals one below the other in such an order that, if any two of them were used for making a cell, the direction of the current in the liquid would be from the one higher in the column to the lower. Such an arrangement is called the *electrochemical series*, and for some of the principal metals it is given here.

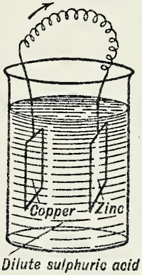


FIG. 34/1

Now although this list is drawn up in connection with what we may call an *electrical* property of the elements concerned, we soon find that it also expresses some of their *chemical* properties. Thus as we descend the series we find that

(1) Any metal will displace a lower metal from a solution of one of its salts, e.g. magnesium will displace zinc from a solution of zinc sulphate, zinc will displace copper and so on. An important special case is that the metals above hydrogen will displace this element from acids [1] (an acid being regarded as a salt of hydrogen), while the metals below it will not.

Potassium
Sodium
Calcium
Magnesium
Aluminium
Zinc
Iron
Tin
Lead
(Hydrogen)
Copper
Mercury
Silver
Gold

---

[1] With lead the action is extremely slow, partly because it is so near hydrogen in the series, but chiefly because the insoluble salts produced (lead sulphate, etc.) protect the lead from further action.

(2) The metals displace hydrogen from water with increasing difficulty (this is evidently closely connected with the special case in (1)). You will find the statement well illustrated in Chapter 9, where the action of potassium, sodium, calcium, magnesium and iron on water is discussed, and where it is mentioned that copper—below hydrogen in the series—does not decompose water at any temperature.

(3) The oxides are reduced with increasing ease. The oxides of the metals down to zinc cannot be reduced by heating in hydrogen, and in this respect they differ from those of iron, tin, lead and copper. Oxides of mercury, silver and gold are reduced by merely heating, no hydrogen being necessary.

With carbon as the reducing agent, the same remarks apply, except that zinc must be added to the list of oxides which can be reduced.

Notice that the metals above zinc have become known only in comparatively recent times. This is because most metals are obtained by reduction of their ores, and the difficulty of the process increases as we ascend the series. The five metals at the top are obtained, not by reduction, but by electrolysis.

(4) The metals oxidise less and less readily (this perhaps is only the last paragraph from another point of view). At the one extreme we have potassium, sodium and calcium, which it is very difficult to *prevent* from oxidising; at the other we have silver and gold, used in coinage because (among other reasons) they do not oxidise on exposure to the air. In fact, metals at the bottom end of the list tend to occur in the free condition.

Iron certainly seems to rust more readily than aluminium, but we must remember that the easy rusting of iron is largely due to the fact that iron rust tends to fall off as fast as it is formed, thus exposing a fresh surface of metal to the action of the air. Aluminium rust sticks tightly on, forming a protective coating over the metal beneath.

(5) The action of heat on the nitrates is worth recalling (p. 340). They are all decomposed, with the formation of nitrates in the case of sodium and potassium, and of oxides as far down as copper. Below copper, as already indicated, the oxides are further decomposed, giving the metal itself.

(6) *Hydroxides and Carbonates.* Those of potassium and sodium are very stable (they are not decomposed by heating with a bunsen), and are very soluble in water. From calcium to copper they are decomposed with increasing ease, and are practically insoluble in water (except calcium hydroxide, which is slightly soluble, giving lime-water). Below copper, these compounds are either extremely unstable, or do not exist at all.

There are some other properties of the metals which are closely related to their position in the electromotive series. It is a good plan to know the list by heart.

Electrolytes. In fig. 34/2 a voltaic cell (or other source of current such as an accumulator) is represented at B by a long stroke and a short one, the current being supposed to flow from long to short as shown. The wires are connected to metal plates A and C (sometimes carbon plates)—the ***electrodes.*** If A and C touch we say that 'the circuit is complete'—a current flows. In fig. 34/2 the electrodes are represented as separated, but dipping into a liquid. Will a current flow? That depends on the nature of the liquid. If it consists of water, for instance, or a solution of sugar, or alcohol, no current will flow. We say that the water, alcohol, etc., are *non-conductors.*

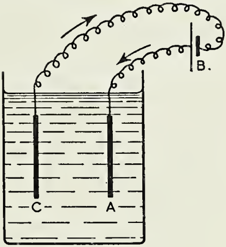


FIG. 34/2

If, however, after dipping the electrodes in water, we add a little hydrochloric acid to the solution, a current begins to flow. Bubbles of gas at once begin to appear at A, where the current enters the solution, and at C, where it leaves it. The bubbles soon rise to the surface and can be collected in test-tubes. On examination, the gas given off from C is found to be *hydrogen,* while that from A turns out to be *chlorine* (actually chlorine is slow to make its appearance because it dissolves, but its presence is easily detected by its bleaching action on a piece of litmus paper held near A).

The solution of hydrochloric acid is evidently acting as a *conductor*. The acid itself is said to be an ***electrolyte***, an electrolyte being a substance which when dissolved in water (or, occasionally, in some other liquid) produces a solution which acts as a conductor. Sometimes a fused substance so acts (cf. pp. 422 and 434).

Electrolysis. It appears that in the process just discussed, the electrolyte is undergoing decomposition. Such a process is known as ***electrolysis***. In carrying out an electrolysis, it is usual to improve in certain ways the very simple apparatus we have so far described. If (as in the case of hydrochloric acid) the substances produced at the electrodes are gases, receivers of some sort would be filled with water and inverted over the electrodes, as shown in fig. 34/3.

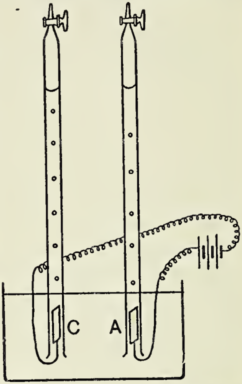


Fig. 34/3. Collecting gases produced by electrolysis

The electrode A (fig. 34/3), at which the current enters the solution, is known as the ***anode***, while that at which it leaves, C, is called the ***cathode*** (sometimes spelt kathode). The cell in which the electrolytic action takes place is known as a ***voltameter***.

We must now try to get a clear idea of what is happening during the electrolysis of hydrochloric acid. It certainly looks as if the acid were being split up by the action of the current. There is good reason to believe, however (though we cannot here go into the evidence), that *the hydrochloric acid was already split up as soon as it was mixed with the water, before the electrodes or wires were introduced at all.*

But a solution of hydrochloric acid does not *bleach* as it would if free chlorine were present, and we certainly do not notice any bubbles of hydrogen. It seems absurd, then, to say that 'the hydrochloric acid was already split up.'

The theory is that the molecule of the gas hydrogen chloride, HCl, consists of a positively charged hydrogen atom combined with a negatively charged chlorine atom, the molecule as a whole being electrically neutral. When these molecules enter water they ***ionise,*** i.e. the charged atoms drift apart. These charged atoms contained in the solution are known as ***ions.*** The word is derived from a Greek word meaning 'wanderers.'

But why does such a solution show no bleaching properties? The answer is simply that the chlorine with which we are familiar consists of *unchanged* atoms (pairs of atoms, to be quite correct), while the ions of which we are speaking consist of *charged* ones. An ion is, in fact, a kind of compound—a compound consisting of an atom + electricity. We may think it is very surprising that when a chlorine atom 'combines' with electricity it should become utterly unlike ordinary chlorine; but after all, a chlorine atom becomes utterly unlike ordinary chlorine when it combines with sodium (forming common salt). The one case is no more surprising than the other. A similar explanation, of course, would account for the fact that a solution of hydrochloric acid shows no sign of containing ordinary hydrogen, although according to the theory it contains hydrogen atoms.

Suppose now that we could treat our solution of hydrochloric acid in such a way that each hydrogen (i.e. hydrogen atom + positive charge) would lose its charge, and similarly each chlorine ion. What would happen then?

Clearly, if our theory is sound, we should have just *ordinary* hydrogen and chlorine. But how can we discharge the ions?

If you have studied elementary electricity you will know that a positively charged body will attract a negatively charged body. Now, when we dip the electrodes into the acid solution we are introducing two bodies which are kept constantly charged by the battery, the anode positively and the cathode negatively (fig. 34/4). The ions are attracted

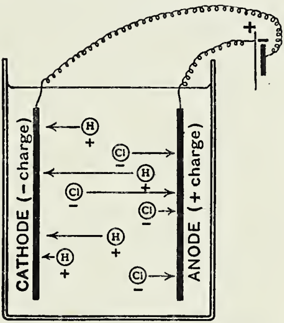


Fig. 34/4. Movement of ions

towards these electrodes—the negatively charged chlorine ions towards the positively charged anode, while the hydrogen ions similarly move towards the cathode. At the anode the negative charge of the chlorine ions is neutralised by the positive charge on the anode. The ions are therefore discharged and *ordinary chlorine* is produced. Similarly, ordinary hydrogen is produced at the cathode. Fresh charges flow from the battery to the electrodes, to make up for what has been lost by the discharging action of the ions (for remember that when a chlorine ion loses a negative charge, the electrode loses an equal positive charge). Thus the current is maintained by the action of the ions, and the liquid acts as a conductor.

So far we have spoken only of the ionisation of hydrogen chloride. Speaking generally, the three great classes of substances known as *acids*, *bases* and *salts* all undergo ionisation in solution.

When we make a further study of valency (p. 507), we shall find frequent mention of a tiny but very definite unit of negative electricity called an *electron*. It is the passage of one of these from a hydrogen atom to a chlorine atom which causes the former to be positively and the latter negatively charged. In fact, instead of H^+ and Cl^-, we sometimes write H^{-e} and Cl^{+e} or Cl^e (for if the hydrogen atom was originally neutral, the loss of *negative* electricity will evidently leave it with a *positive* charge).

When sulphuric acid ionises we have *two* charged hydrogen atoms, H^+, H^+ (or H^{-e}, H^{-e}). To balance these, the sulphate group carries *two* unit charges, i.e. it is SO_4^{--} ($SO_4^{=}$), or SO_4^{+2e}. We can generalise by saying that any ion will carry a number of unit charges (or electrons) corresponding to its valency. Thus copper will be Cu^{++}, or Cu^{-2e}.

In this chapter we have frequently spoken of positively charged and negatively charged bodies, but it is well to keep close to the idea that we are concerned all the time with

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[1] Probably the ion is hydrated, i.e. it is not H^+ but H_3O^+ ('hydroxonium'), and similarly with solutions of other acids. However, as the final result is the same, we shall continue for simplicity to speak of H^+.

electrons. The cathode with its negative charge is a conductor with an excess of electrons, while the anode has a deficiency. Chlorine atoms are constantly conveying electrons to the anode (becoming ordinary chlorine atoms as they 'hand over'), while hydrogen ions are at the same time removing electrons from the cathode. Thus we have a flow of *electrons* from the anode, through the battery to the cathode, while the circuit is completed in the liquid by two gangs of porters so to speak, consisting of hydrogen ions and chlorine ions respectively. Members of the first gang are constantly removing electrons from the cathode, while members of the second are depositing them at the same rate at the anode. The electron current is, of course, in the opposite direction to the 'ordinary' current, because the electrons are negative charges, and negative electricity travelling in one direction corresponds to positive electricity travelling in the opposite one.

Before dealing with some particular cases of electrolysis, we had better consider just a little more 'theory,' which can conveniently be expressed in the form of two rules.

Rule 1. *If a solution to be electrolysed contains more than one cation* (i.e. the positively charged ion, which moves towards the cathode, as H^+ in fig. 34/4), *these will ordinarily be discharged in the order of the electrochemical series* (p. 391), *beginning with the lowest.* E.g. if the ions of copper, hydrogen and sodium are all present, Cu^{++} will be discharged before H^+, and H^+ before Na^+.

Our 'rule' will now and then lead us astray, because it ignores certain qualifications which are considered in a full treatment of the subject.

Anions also have their place in the electrochemical series, though they are not shown in the list on p. 391; and the rule applies equally to them. Actually, however, the only anions we shall meet with in our present studies are chloride (Cl^-), hydroxide or hydroxyl (OH^-) and sulphate ($SO_4^=$). They are usually discharged in the order just given, i.e. chloride before hydroxide, and hydroxide before sulphate. This is not quite the 'electrochemical' order (in which OH^- would come before Cl^-). The disturbance is due to the fact that in the cases we shall consider, the concentration of the chloride ion is usually enormously greater than that of the hydroxide ion. When the former concentration is greatly reduced, the 'electrochemical' order is followed, i.e. the hydroxide ion is discharged first.

Rule 2. For each atom or group of atoms liberated at the anode, equivalent atoms or groups will be liberated at the cathode.

Suppose, for instance, an atom of oxygen is liberated at the anode. At the cathode *two* atoms of hydrogen will be liberated, or *one* atom of copper, etc. (because the *equivalent* of one atom of oxygen is two atoms of hydrogen, or one atom of copper).

It is worth while to consider the reason for this second rule. Let us go back to the electrolysis of hydrochloric acid, HCl. We saw that when this substance is ionised, the hydrogen atom loses an electron, becoming H^{-e}, while the chlorine atom gains one, becoming Cl^{+e}. Now when Cl^{+e} touches the anode it loses its electron (becoming Cl), *which electron may be supposed to travel through the wire and battery to the cathode.* When H^{-e} touches the cathode it acquires an electron, becoming H. If n hydrogen ions are discharged, n electrons will be required, and to supply these, n chlorine ions must have been discharged.

Similarly, the discharge of one copper ion, Cu^{-2e}, at the cathode would require the discharge of *two* chlorine ions, $2Cl^{+e}$, at the anode.

We are now in a position to discuss some particular cases of electrolysis.

Water. With pure water there is practically no action. This is because there are not sufficient ions present to carry any appreciable current, and so for practical purposes there is a gap between the electrodes.

On adding sulphuric acid, however, we introduce a good supply of ions—for sulphuric acid is completely ionised in solution—each molecule giving rise to H^+, H^+ and $SO_4^=$. These ions carry the current, and we soon have a large number of hydrogen ions round the cathode, and of sulphate ions round the anode. At the cathode, hydrogen ions are discharged as already discussed on p. 396, and ordinary hydrogen is evolved as a gas. At the anode the situation is more complicated. Here we have (i) a comparatively small number of hydroxide ions, OH^-, derived from the (very slightly ionised) water, and (ii) a large number of sulphate ions, $SO_4^{=}$. Because of the position of hydroxide in the electromotive series, *it is the hydroxide ions which are discharged.* The discharged ions then give rise to water and oxygen. Considering four such ions, we have $4OH^- \rightarrow 4OH \rightarrow 2H_2O + O_2$. This molecule, O_2, is liberated at the anode. Rule 2 above reminds us that the corresponding amount of hydrogen liberated at the cathode will be 4H, giving $2H_2$. Thus two molecules of hydrogen are liberated for every one of oxygen, exactly as though the water only were undergoing change. There is no change in the amount of sulphuric acid.

But here we must recall that water is ionised only to an extremely small extent ($H_2O \rightleftharpoons H^+ + OH^-$)—about one molecule in every 550 *millions*! The question at once arises, 'How could such a small number of hydroxide ions serve to discharge all the electricity which has been carried by the numerous sulphate ions?' The answer is that the moment we disturb the equilibrium $H_2O \rightleftharpoons H^+ + OH^-$ by the removal of hydroxyl ions, fresh molecules of water ionise in an attempt to restore it. Thus, though at any one instant the supply of hydroxide ions is only small, this supply never runs out.

We see then that the ions which are *discharged* at an electrode are not necessarily the same as those mainly concerned in *carrying the current*,—an important point to remember.

In the above discussion we have supposed platinum electrodes to be used, and these are unaffected by oxygen or hydrogen. An interesting case arises if *lead* electrodes are employed. The anode soon turns brown, as the lead combines with oxygen, forming lead dioxide. Any film of lead oxide on the cathode is reduced to lead. The action of the accumulator or storage cell is to a certain extent related to the chemical changes just mentioned.

Where cheap electric power is available, the 'electrolysis of water' is carried out on a considerable scale for the preparation of pure hydrogen (p. 147). Caustic soda or potash is usually employed instead of sulphuric acid, one advantage being that a product free from carbon dioxide is obtained. Round the cathode we have numerous Na^+ ions (if caustic soda is used), and a few H^+ ions (from the water). It is the latter which are discharged in preference to the Na^+ ions, because hydrogen is below sodium in the electrochemical series. Round the anode we have only OH^- ions, one of which is discharged for each H^+ ion (Rule 2). The net result is evidently the same as if water alone were being electrolysed; and the amount of sodium hydroxide in solution is unchanged.

Sodium Sulphate, Na_2SO_4. This is completely ionised ($Na_2SO_4 = 2Na^+ + SO_4^=$), and almost all the current is carried by the sodium ions moving towards the cathode, and the sulphate ions moving in the opposite direction. Round the cathode we have sodium ions, Na^+, together with a few hydrogen ions, H^+, from the water, but for the reason already mentioned it is the latter which are discharged. At the anode we have sulphate ions and hydroxide ions, the latter being discharged and oxygen evolved. The net result is that we have the 'electrolysis of water' once more, sodium sulphate, unchanged in quantity, remaining in solution.

Notice, however, that because hydrogen ions are being discharged at the cathode, an excess of hydroxide ions, OH^-, will remain in the neighbourhood, i.e. round the cathode the liquid will be *alkaline* to litmus. Similarly, in the neighbourhood of the anode, the liquid will be *acid* owing to the excess of hydrogen ions. On stirring, the liquid becomes neutral.

Hydrochloric Acid, HCl. We have already discussed this, but without taking any account of the H^+ and OH^- ions derived from the water.

The only cation present is hydrogen, H^+ (derived mainly from the completely ionised acid, but to a very small extent from the water). The anions are OH^- (from water) and Cl^- (from the acid).

Clearly hydrogen will be given off at the cathode. At the anode, Cl^- is discharged in preference of OH^- because of its much greater concentration (p. 397), giving rise to unchanged atoms of chlorine, which pair off, forming molecules of Cl_2. This dissolves freely in the water, and until the latter is saturated very little can be collected.

This is the usual result, but with *very dilute* hydrochloric acid, OH^- begins to be discharged and oxygen to be produced instead of chlorine. (Cf. top of p. 398.)

A *carbon* anode should be used, as platinum is attacked to some extent by chlorine. The same applies in the electrolysis of a solution of sodium chloride.

Sodium Chloride, NaCl. So far as the cathode is concerned, the case is the same as that of sodium sulphate already discussed, hydrogen being evolved. At the anode, chlorine is liberated (but dissolved), as in the case of hydrochloric acid.

The solution contains sodium ions, Na^+, unchanged in quantity. Further, since only hydrogen ions have been removed from the water, we are left with an excess of OH^- ions. But Na^+ and OH^- are the ions of sodium hydroxide, NaOH, and so for practical purposes we are left with a solution of this substance.

If a *very dilute* solution of sodium chloride is used, oxygen is evolved at the anode (as in the case of very dilute hydrochloric acid), and hydrogen at the cathode. Thus the result is the same as in the case of the 'electrolysis of water,' unchanged sodium chloride remaining in solution. In practice, such a result is not likely to be fully realised. The oxygen would be mixed with some chlorine, and the solution would be found to contain some sodium hydroxide.

Copper Sulphate, $CuSO_4$. (i) *Platinum electrodes.* The cations present are H^+ (from the water) and Cu^{++}. It is the latter which are discharged, because copper is below hydrogen in the electrochemical series.

The anions are $SO_4^=$ and OH^-. The situation at the anode is the same as in the electrolysis of water to which sulphuric acid has been added, and oxygen is evolved.

As the process continues, the remaining ions consist to an increasing extent of H^+ and $SO_4^=$, i.e. sulphuric acid is produced. When the point is reached at which all the copper has been deposited, we are left with a colourless solution of sulphuric acid, and we now continue with the 'electrolysis of water.'

(ii) *Copper electrodes.* The action at the cathode is the same as just discussed, copper being deposited.

At the anode there are three possible actions: (*a*) discharge of OH^- ions, (*b*) discharge of $SO_4^=$ ions, (*c*) conversion of copper, Cu, into copper ion, Cu^{++}, i.e. gradual solution of the anode. Of these three, it is the last which requires the least amount of energy, and which therefore takes place.

Thus, in the final result, copper is steadily removed from the anode and added at an equal rate to the cathode, the amount of copper sulphate in solution remaining constant. For all practical purposes the effect is as though copper 'travelled' from anode to cathode.

These results have found a number of practical applications.

Purification of Copper. A slab of impure copper is used as the anode (illustration, p. 463), while the cathode consists of a thin plate of the pure metal ('starting sheet,' illustration p. 464), both anode and cathode being suspended in a bath of acidified copper sulphate solution. The cathode becomes thicker (with pure copper) at the expense of the anode. Some of the impurities in the latter are deposited on the floor of the bath as *anode mud* or *anode slime.* These impurities include lead, silver and gold. Metals higher in the electrochemical series (e.g. iron and zinc) pass into solution.

Making Electrotypes. It is often necessary to obtain duplicates of type which has been 'set up,' because if a very large number of copies were printed off the original type, the latter would become worn and the print obtained from it would be blurred.

To obtain a duplicate, the type as originally set up is pressed upon a bed of wax or lead, a mould being thus obtained. The mould is dusted over with powdered graphite, which is a good conductor of electricity. The 'black-leaded' mould is now hung as cathode in a bath of acidified copper sulphate solution, a plate of copper being made the anode. Copper is deposited until it is considered to be sufficiently thick. After this the copper deposit, which is an exact reproduction of the original type, is carefully stripped off, backed with a suitable lead alloy and mounted flat upon a wooden block.

Copies of metals and many other objects may be made in a similar way.

Electroplating. If a small metal object (e.g. a spoon) were made the cathode in the electrolysis of copper sulphate, it would receive a coating of copper. Probably there would be very little sale for copper-plated spoons, but silver plating may be carried out by a quite similar method. In this case a silver anode is used, and the bath consists of a solution of a silver salt instead of a copper one. (Actually a solution of silver cyanide in potassium cyanide is employed.) Nickel plating and gold plating are effected by very similar methods. Bathroom taps, the radiators of motor-cars, etc. are often electroplated with chromium, a metal which does not easily tarnish.

Some of the most important applications of electrolysis, however, are met with in the extraction of the metals, and we shall come across several cases in connection with sodium (pp. 416, 422) and zinc (p. 455).

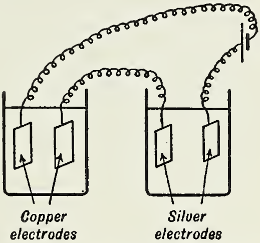

FIG. 34/5. Finding equivalents by electrolysis

Finding Equivalents by Electrolysis. Suppose the *same current* is passed through a solution of silver nitrate containing silver electrodes, and one of copper sulphate containing copper electrodes. By weighing the silver cathode before and after the experiment the amount of silver deposited can be determined, and in a similar way we can find the amount of copper deposited. It has been observed that

$$\frac{\textit{wt. of silver deposited}}{\textit{wt. of copper deposited}} = \frac{\textit{chemical equivalent of silver}}{\textit{chemical equivalent of copper}}$$

This result ought not to surprise us very much if we remember that 'the same current' implies that we have the same number of electrons taking part at each electrode, and for every two electrons we have the deposit of one atom of copper ($Cu^{-2e} + 2e = Cu$), or of two atoms of silver ($2Ag^{-e} + 2e = 2Ag$). Recalling that (i) 108 and 64 are the atomic weights of silver and copper respectively, and that (ii) chem. equivalent $=$atomic wt. $\div$ valency, we have

$$\frac{\textit{wt. of silver}}{\textit{wt. of copper}} = \frac{2 \times 108}{64} = \frac{108}{64 \div 2} = \frac{\textit{chem. equiv. of silver}}{\textit{chem. equiv. of copper}}$$

Such a result is true not only for silver and copper, but is a general one. It is expressed in Faraday's ***Second Law of Electrolysis***,[1] viz.: '*If solutions of several electrolytes are arranged in series and the same electric current is passed through them, the weights of the various ions deposited are proportional to their chemical equivalents.*'

We can evidently make use of this law to find the equivalent of the other elements provided we know the equivalent of one. Consider the following example:

An electric current was passed through three voltameters in series containing respectively copper sulphate solution, silver nitrate solution and water acidified with sulphuric acid. It was found that after the current had passed for a certain time 0·186 *gm. of copper and* 0·632 *gm. of silver had been deposited on their respective cathodes, and that* 70·5 *c.c. of hydrogen, measured at* 15° *C. and* 74 *cm. pressure, had been liberated. Calculate the equivalent weights of copper and of silver.* (1 *litre of hydrogen at N.T.P. weighs* 0·09 *gm.*)

We must first find the weight of the hydrogen.

$$\text{Vol. at N.T.P.}=70{\cdot}5\times\frac{273}{288}\times\frac{74}{76}=65{\cdot}1 \text{ c.c.}$$

$$\therefore \text{ wt. of hydrogen}=\frac{90{\cdot}0}{1000}\times 65{\cdot}1=0{\cdot}00586 \text{ gm.}$$

Now if c=chemical equivalent of copper, we have

$$\frac{\text{wt. of copper}}{\text{wt. of hydrogen}}=\frac{\text{chemical equivalent of copper}}{\text{chemical equivalent of hydrogen}}.$$

$$\therefore \frac{0{\cdot}186}{0{\cdot}00586}=\frac{c}{1}. \qquad \therefore c=\frac{0{\cdot}186}{0{\cdot}00586}=\boldsymbol{31{\cdot}7}.$$

Similarly

$$\frac{\text{wt. of silver}}{\text{wt. of hydrogen}}=\frac{\text{chemical equivalent of silver}}{\text{chemical equivalent of hydrogen}}.$$

$$\therefore \frac{0{\cdot}632}{0{\cdot}00586}=\frac{s}{1}. \qquad \therefore s=\boldsymbol{107{\cdot}9}.$$

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[1] The First Law is as follows : *The quantity of a substance liberated at an electrode of a voltameter is proportional to the quantity of electricity which has passed, i.e. to the product* (*current*) × (*time*).

Strong and Weak Electrolytes. In the course of this chapter we have often had occasion to notice that water undergoes ionisation only to an extremely small extent. It is said to be an extremely *weak* electrolyte, 'weakness' or 'strength' in this connection indicating the extent to which ionisation takes place. Other weak electrolytes (though not nearly so weak as water) are many of the organic acids (e.g. carbonic acid and acetic acid), and a solution of ammonia in water. Sugar and alcohol would be examples of non-electrolytes.

On the other hand, some substances are completely ionised in solution and are known as *strong* electrolytes. They include the common inorganic acids (sulphuric, hydrochloric, nitric), which are therefore known as *strong acids*, and the bases sodium hydroxide and potassium hydroxide ('strong bases'). Most salts are also strong electrolytes.

A salt derived from a strong base and a weak acid (e.g. sodium carbonate, derived from sodium hydroxide and carbonic acid) gives a solution alkaline to litmus. Let us see why. First the salt ionises ($Na_2CO_3 = 2Na^+ + CO_3^=$). The carbonate ion combines with hydrogen ion from the water, forming the weak electrolyte carbonic acid ($2H^+ + CO_3^= \rightleftharpoons H_2CO_3$). This withdrawal of hydrogen ions upsets the equilibrium $H_2O \rightleftharpoons H^+ + OH^-$. More water ionises to restore it, and so the process goes on until a new equilibrium is reached. Corresponding to the hydrogen ions removed by combination with carbonate ions, hydroxide ions accumulate in the solution, which therefore reacts alkaline. Similarly, a salt derived from a weak base and a strong acid (e.g. copper sulphate) will give an acid solution.

Formation of Precipitates. In a chapter concerned so much with ions, it will be convenient to consider briefly the question of the formation of precipitates.

It is commonly said that silver chloride, AgCl, is insoluble in water. For most practical purposes we may regard this statement as true, but actually no substance is *absolutely* insoluble. Silver chloride, for instance, dissolves to the extent of about 1½ parts by weight in a million parts of water, and the dissolved part would be completely ionised.

Now suppose we were to add, say, a deci-normal solution of silver nitrate (p. 484) to a similar solution of sodium chloride. In the former solution the concentration of silver ion would be thousands of times what it would be in the silver chloride solution. Similarly, the concentration of the chloride ion in the sodium chloride solution would be thousands of times its concentration in the silver chloride solution. We have mixed the two solutions and four kinds of ion are now present, Ag^+, NO_3^-, Na^+ and Cl^-. What will happen?

The concentration of silver ion and of chloride ion will at once be reduced to what it would be in a saturated solution of silver chloride, i.e. to something near zero. This result would be secured by the *precipitation* of silver chloride.

Similarly, barium sulphate ('insoluble') can give only an extremely low concentration of barium ion, Ba^{++}, and sulphate ion, $SO_4^=$. If, therefore, we add a solution of a barium salt (e.g. the chloride, $BaCl_2$) to a solution of a sulphate (e.g. sodium sulphate, Na_2SO_4), we shall have barium sulphate precipitated. The principle is a general one, and as a rough working rule we may say that if two solutions contain between them the ions C^+, A^-, of a comparatively insoluble salt CA, then on mixing the solutions CA will be precipitated.

The formation of precipitates is useful to the chemist in a number of ways. Three of these may be summed up in the words *detection*, *removal* and *estimation*.

Detection. We have had several examples of this, e.g. detection of chloride by the production of a precipitate of silver chloride (p. 246). On p. 476 we shall see how the presence of a lead compound in drinking-water could be detected by the production of a precipitate of lead sulphide.

Removal. We had an example on p. 310, where we saw how copper could be removed (as a precipitate of copper sulphide) from a mixture containing compounds of copper, zinc and sodium.

Estimation. As an example, suppose we are required to find the percentage of sodium sulphate in a mixture of sodium sulphate and sodium chloride.

We weigh out, say, 3 gm. of the mixture, dissolve in water and add excess of barium chloride. All the sulphate is precipitated as barium sulphate. This is filtered off, washed, dried and weighed. Suppose it weighs 1·71 gm.

Now the molecular weight of barium sulphate, $BaSO_4$, is $137+32+64=233$, and of this, $32+64$, or 96, is 'sulphate,' SO_4. The amount of *sodium* sulphate, Na_2SO_4, corresponding to this, is $46+96=142$. Evidently 142 gm. of sodium sulphate gives rise to 233 gm. of barium sulphate.

Here we have 1·71 gm. of barium sulphate, so the weight of sodium sulphate must have been $\frac{142}{233} \times 1{\cdot}71 = 1{\cdot}04$ gm. This was present in 3 gm. of the mixture, so the percentage of sodium sulphate is $\frac{1{\cdot}04}{3} \times 100 = 34{\cdot}7$.

Questions

N.B. *See note in italics*, p. 132

1. What is the action, if any, when: (i) a rod of zinc is placed in a solution of lead nitrate; (ii) a rod of copper is placed in a solution of lead nitrate? Give a brief explanation of your answers. *J.M.B. (part)*

2. Compare and contrast the properties of iron, lead and calcium, using as illustrations their reactions with (*a*) water (or steam); (*b*) oxygen; (*c*) dilute hydrochloric acid.

Arrange the following metals in order of their chemical activity, placing the most active first: iron, lead, calcium, zinc, copper, sodium. *Camb.*

3. Define the terms *ion*, *cathode*, *electrolyte*.

Explain carefully what happens when an electric current is passed through a dilute solution of sulphuric acid between platinum electrodes. What ions are present in a solution of (*a*) aluminium sulphate; (*b*) calcium nitrate; (*c*) sodium sulphite? Indicate the charge on each ion. *Camb.*

4. Explain what happens when a direct current is passed through (*a*) a *very dilute* solution of common salt between platinum electrodes; (*b*) a *strong* solution of common salt between carbon electrodes.

A silver voltameter is connected in series with a copper voltameter. What weight of silver will be deposited in one voltameter whilst 0·16 gm. of copper is deposited in the other? *Lond.*

5. What will be evolved from, or deposited on, each electrode of cells connected in series and containing

(*a*) dilute sulphuric acid and platinum electrodes;
(*b*) copper sulphate and copper electrodes;
(*c*) sodium sulphate and platinum electrodes;
(*d*) fused sodium chloride with an iron cathode and a carbon anode?

When 1000 c.c. of hydrogen at N.T.P. are evolved in (*a*), what will be the volumes of gases or weights of solids, if any, liberated at each of the other electrodes? *Oxf.*

6. Describe and explain what happens when, using platinum electrodes (*a*) sodium hydroxide solution, (*b*) copper sulphate solution, is electrolysed.

Explain how sodium is manufactured by electrolysis. *O.C.*

7. Describe and explain what happens when, using platinum electrodes, a direct current of electricity is passed through a solution of copper sulphate until some time after the solution has become colourless.

Outline the method for purifying crude copper by electrolysis. State *two* other industrial uses for electrolysis. *Camb.*

8. Define the Equivalent Weight of an element. How is the Equivalent Weight related to the Atomic Weight?

An element M has an atomic weight of 27 and an equivalent weight of 9. Write down the formula for its oxide and its sulphate.

An electric current was passed through two voltameters in series containing respectively copper sulphate solution and water rendered slightly acid by sulphuric acid. After the current had passed for a certain time 0·248 gm. of copper had been deposited on the cathode and 94 c.c. of hydrogen, measured at 15° C. and 740 mm. pressure had been liberated. Calculate the Equivalent Weight of copper.

(1 litre of hydrogen at N.T.P. weighs 0·09 gm.) *Lond.*

9. What current must be passed through a solution of copper sulphate to deposit 5·4 gm. of copper on the cathode in 30 minutes?

(Electrochemical equivalent of copper[1] = 0·0003 gm./coulomb.)
Camb. (*part*)

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[1] The electrochemical equivalent of an element (copper in this case) is the number of grams of it liberated per second by a current of 1 ampere.

But the quantity of electricity conveyed by a current of 1 ampere in 1 second is known as a *coulomb*, so we may define the electrochemical equivalent of an element as the number of grams of it liberated by 1 coulomb.

10. State Faraday's laws of electrolysis.

Using an electrolytic method, how would you determine the weight of copper sulphate in a litre of a dilute solution of this salt?

In such an experiment where platinum electrodes were used, the weight of the cathode increased by 4 gm. What volume of gas at 17° C. and 750 mm. could be collected at the anode? *Camb.*

11. Explain what happens when a direct current is passed through:

(*a*) dilute sulphuric acid between platinum electrodes;
(*b*) aqueous caustic soda between platinum electrodes;
(*c*) copper sulphate solution between copper electrodes.

What *total* volume of gas, measured at N.T.P., would be liberated from dilute sulphuric acid by the current which, flowing for the same time, deposits 0·315 gm. of copper from copper sulphate solution?

(Gram molecular volume = 22·4 litres at N.T.P.; H = 1, Cu = 63.)
Lond.

CHAPTER 35

METALS AND NON-METALS

Most people in a rough sort of way can distinguish between 'metals' and 'non-metals.' They would decide, for instance, that copper, silver and lead are metals, and that charcoal, sulphur and oxygen are non-metals. If we asked them how they distinguished between the two classes they would most likely answer that a metal has a peculiar 'shine' or lustre that a non-metal does not possess.

That is, in fact, a useful means of distinguishing. We might notice a few others. Metals are usually good conductors of heat and electricity, while non-metals are not. A piece of sulphur conducts heat so badly that if you hold a roll of it firmly in your warm hand you can hear it cracking. You can easily reason out for yourself why this little experiment proves that sulphur is a bad conductor of heat.

Metals are often 'sonorous,' i.e. they give out a ringing sound when struck. They usually have a high melting-point, and in fact only one of them (mercury) is a liquid at ordinary temperatures. Those non-metals that are solid at ordinary temperatures (e.g. sulphur and phosphorus) usually have low melting-points, and many non-metals (oxygen and nitrogen, for instance) have melting-points so low that at ordinary temperatures they are gases. Metals usually have a rather high density and non-metals a low one. Metals are more or less malleable and ductile, while non-metals are brittle.

You can easily think of exceptions to the rules just mentioned. Graphite 'shines,' for instance—that is why it is used for blackleading grates. Lead is not sonorous, charcoal has an extremely high melting-point, and sodium has a density so low that it will float on water. At the same time the distinctions we have mentioned hold good in the majority of cases.

Chemical Differences. The points discussed so far are all concerned with *physical* properties. We must now consider the *chemical* properties which distinguish metals from non-metals.

Much the most important is that *metals give rise to basic oxides, non-metals to acid-forming oxides.* We will not say much more about this, because it has already been discussed at some length on pp. 150–152.

Closely connected with the general rule that

$$basic\ oxide + acid = salt + water$$

is the fact that, in many cases

$$metal + acid = salt + hydrogen$$

If you write out the equations for the action of sulphuric acid on zinc oxide and on zinc respectively, you will see quite clearly what is meant. Hydrogen is not given off, however, in the case of those metals, such as copper, which are below hydrogen in the electrochemical series (p. 391).

Besides the oxides, there are two other groups of compounds which are well worth considering in our comparison of metals and non-metals. They are the *chlorides* and the *hydrides.* The chlorides have already been discussed on p. 367, where it was pointed out that chlorides of non-metals are usually readily hydrolysed by water, while chlorides of metals are not.

Non-metals usually form stable compounds with hydrogen. Thus water (H_2O), ammonia (NH_3), hydrogen sulphide (H_2S), hydrogen chloride (HCl) and methane (CH_4) are the hydrides of oxygen, nitrogen, sulphur, chlorine and carbon respectively. These hydrides are either *gases* or *liquids which can easily be vaporised.* They are not decomposed by water.

Metals seldom form hydrides.[1] When they do, the hydrides are *solids* easily decomposed by water. Thus calcium forms a solid hydride CaH_2, which is readily decomposed by water, giving hydrogen

$$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2$$

(Under the name *hydrolith,* this hydride has sometimes been used as a source of hydrogen for filling balloons, etc.)

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[1] The only common metals which form well-defined hydrides are sodium, potassium and calcium.

Finally, *electrolysis* enables us to classify most of the elements as metals or non-metals. Metals are electropositive, and may be deposited *alone* at the cathode. A non-metal never appears at the cathode except, occasionally, *in conjunction with some other element* (e.g. if a solution of ammonium chloride NH_4Cl were electrolysed, the non-metal nitrogen would appear at the cathode, but it would be in conjunction with hydrogen).

It will help to straighten out our ideas if we apply them to a particular case, so let us consider the reasons which cause us to regard copper as a metal and graphite as a non-metal.

Copper has the characteristic metallic lustre. It is a good conductor of heat and electricity, is sonorous, has a high melting-point and a high density. It is very malleable and ductile.

We now come to its chemical properties. It forms a basic oxide,—cupric oxide easily dissolves when warmed with dilute sulphuric acid, forming copper sulphate and water only ($CuO + H_2SO_4 = CuSO_4 + H_2O$). Cupric chloride, $CuCl_2$, is only very slightly hydrolysed by water. The existence of a hydride is doubtful. In any case, the compound suspected of having the formula CuH_2 is a solid, indicating that it is the hydride of a *metal*. In electrolysis copper is often deposited by itself at the cathode.

On the other hand, copper does *not* give off hydrogen when acted upon by a dilute acid. In this respect we have just a hint of non-metallic properties. (*N.B.* As we descend the electrochemical series we may think of the metals as becoming not simply less electropositive, but more electronegative; i.e. they are becoming more akin to the non-metals.)

It must be admitted that graphite possesses many of the physical properties of a *metal*. It has considerable 'metallic lustre,' is a good conductor of heat and electricity, and has a very high melting-point. It is not sonorous, however, and is neither malleable nor ductile. Its density (2·25) is less than that of aluminium (2·70).

Its oxide, CO_2, is acidic. It does *not* form salts with acids, and *does* form salts when passed into solutions of alkalis (e.g. $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$). It forms many stable gaseous hydrides (e.g. CH_4, C_2H_4, C_2H_2) which are not decomposed by water. In the course of electrolysis it is never deposited at the cathode.

On the other hand, its chloride, CCl_4, though liquid at the ordinary temperature, is not easily hydrolysed by water.

You may at some time, as a practical exercise, be asked to decide whether a given substance (which you are told is an element) is a metal or a non-metal. To increase your difficulties, the substance is supplied in the form of a powder, making it difficult or impossible to say much about its metallic lustre (or absence of it), heat conductivity, etc.

An easy beginning would be to warm the substance with dilute hydrochloric acid. If it dissolves, giving off hydrogen, it is certainly a metal. You could then evaporate the solution and would no doubt obtain a salt-like chloride.

It is very desirable, however, to obtain and examine the oxide. To make this, you could heat a little of the substance in a test-tube with nitric acid. If a metal has been given, this treatment would yield the nitrate, which on stronger heating would give the oxide. A non-metal, however, would not give a very convincing result. It would be better in that case to heat the substance in a deflagrating spoon in a jar of air, or preferably of oxygen.

Having in one way or another prepared your oxide, you shake it up with litmus solution. If this turns blue, the original substance was a metal; if red, a non-metal.

But a solid oxide (probably basic) may be insoluble in water, and so litmus would not be affected. Dissolve it in dilute acid and evaporate. A salt-like residue indicates that the oxide was indeed basic, and so the original powder was a metal.

We may conclude this chapter by noting that the distinction between metals and non-metals is not a sharply defined one—the one class shades off into the other. In the case of copper and carbon the balance of evidence was clear enough, but in some cases (e.g. arsenic) there is just about as much to be said on one side as on the other, and it is impossible to decide whether the element is a metal or a non-metal. Such elements are often called *metalloids*.

Questions

1. By what physical properties can we usually distinguish metals from non-metals? In what respects are lead, sodium and charcoal exceptions to the general rules?

2. What differences in *chemical* behaviour distinguish the metals from the non-metals? Explain clearly why it is that the chemist regards calcium as a metal and phosphorus as a non-metal but finds hydrogen difficult to classify. *Lond.*

3. What is a hydride? Give the name and formula of *one* hydride of each of the following: oxygen, phosphorus, calcium, sulphur, carbon. What can usually be said about an element that forms a hydride?

4. 'The chlorides of non-metals are usually hydrolysed by water, while chlorides of metals are not.' Illustrate from the cases of phosphorus and sodium.

5. The elements mercury and calcium are classified as metals and sulphur and silicon as non-metals. Give reasons to justify these classifications. *Dur.*

6. If you were given a specimen of an element in the form of a powder, what *two* experiments would you perform to find out whether it were a metal or a non-metal? Describe the experiments. Explain your reasons for choosing them, and state the results you would expect, if the specimen were (i) a metal; (ii) a non-metal. *Camb.*

CHAPTER 36

SODIUM, POTASSIUM, CALCIUM

In this chapter and the two next we shall deal (in some cases very briefly) with nine metals and some of their compounds. It will be convenient on the whole to consider them in the order in which they occur in the electrochemical series (p. 391), except that we shall take sodium before potassium, and copper before lead.

SODIUM AND COMPOUNDS

Sodium Chloride. We put this first because, with the exception of the nitrate, it is the only sodium compound which occurs on a really large scale in Nature. Its chief properties have already been described on p. 238, and here we shall add only one point—i.e. it does *not* when pure absorb atmospheric moisture, in spite of the fact that the domestic supply is often found to 'cake.' This caking is due to the presence of small quantities (1 per cent. or so) of magnesium and calcium chlorides, which are very deliquescent. Patent table salts, guaranteed to keep their fine powdery form, are sometimes prepared by adding a calculated quantity of sodium bicarbonate. This reacts with the calcium chloride (and similarly with the magnesium chloride):—

$$CaCl_2 + 2NaHCO_3 = CaCO_3 + H_2O + 2NaCl + CO_2$$

The only impurities present in the table salt are therefore a little calcium carbonate (or powdered chalk), which does not absorb moisture, and the very similar magnesium carbonate.

Sodium Hydroxide, NaOH, is now chiefly prepared from brine by electrolysis. The theory of the process has already been explained on p. 401.

On a manufacturing scale, a 'diaphragm cell' is often employed. Fig. 36/1 shows one of cylindrical shape. The asbestos diaphragm is supported on the outside by a screen of iron gauze, kept wet by the brine which soaks through the asbestos. The solution of sodium hydroxide, produced as already explained (p. 401), runs out at the base of the diaphragm as shown. It contains a large quantity of unchanged sodium chloride, most of which is recovered when the liquid is evaporated to obtain solid sodium hydroxide. This evaporation is carried out in large direct-fired pots, but not until the solution of caustic soda has first been concentrated in vacuum evaporators.

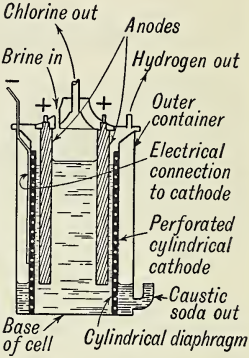

FIG. 36/1. Sodium hydroxide from brine (diaphragm cell)

By courtesy of Encyc. Brit.

An older method of preparation is still employed to a certain extent, and consists in boiling slaked lime with sodium carbonate:—

$$Ca(OH)_2 + Na_2CO_3 = 2NaOH + CaCO_3$$

The process is easily illustrated in the laboratory, and it is complete when, after allowing the insoluble material to settle, a small quantity of the clear liquid no longer effervesces with hydrochloric acid. This indicates, of course, that all the sodium carbonate has been used up. If a fairly generous excess of slaked lime is used the small-scale reaction is complete in five or ten minutes.

Sodium hydroxide, usually bought in the form of white sticks, is a very deliquescent substance (notice how a stick of it 'sweats' after even a few seconds' exposure to the air). It is therefore sometimes used for drying gases—especially ammonia, which reacts with the more usual drying agents.

As is usually the case with a deliquescent substance, it is extremely soluble in water. Much heat is produced at the same time. The solution is strongly alkaline to litmus. It feels slimy, and has a corrosive action on the skin, filter-paper, etc.—hence the common name 'caustic soda.'

Sodium hydroxide is an excellent example of a base, for it easily reacts with an acid, producing a salt and water only. Thus with hydrochloric acid we have

$$NaOH + HCl = NaCl + H_2O$$

The reactions with nitric acid and sulphuric acid are very similar, except that in the latter case either the *normal* sulphate, Na_2SO_4, or the *acid* sulphate, $NaHSO_4$, may be formed according to the relative amounts of sodium hydroxide and sulphuric acid taken (p. 298).

As sodium hydroxide reacts so readily with acids, it is not surprising to find that it also reacts with anhydrides (i.e. acid-forming oxides). Thus it quickly absorbs carbon dioxide, and you will remember that a solution of sodium hydroxide was used for removing this gas from carbon monoxide:—

$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$

If we continue to pass in carbon dioxide after all the hydroxide has been turned into carbonate, the *bicarbonate* is formed. This remains in solution.

$$Na_2CO_3 + H_2O + CO_2 = 2NaHCO_3$$

With sulphur dioxide (i.e. sulphurous anhydride) the action is similar, sodium sulphite, Na_2SO_3, being first formed, and later sodium bisulphite, $NaHSO_3$.

Closely connected with this tendency to react with an acidic oxide, is the well-known fact that the stopper of a bottle containing sodium hydroxide solution is often found to be stuck fast. This is chiefly because of the action of the solution on the silica contained in the glass, the stopper being united to the bottle by a continuous layer of sodium silicate:—

$$2NaOH + SiO_2 = Na_2SiO_3 + H_2O$$

It is worth noting that the only elements which form *soluble* hydroxides are those near the top of the electrochemical series, i.e. (so far as we are concerned) potassium, sodium and calcium, the last being only slightly soluble. The radical ammonium, NH_4, also forms a soluble but very unstable hydroxide.

Hence, as a general rule, when sodium hydroxide is added to a solution of a salt of some other metal, the hydroxide of that metal, being insoluble, is *precipitated*. On adding it to a solution of ferric chloride, for instance, ferric hydroxide appears as a brown precipitate:—

$$FeCl_3 + 3NaOH = 3NaCl + Fe(OH)_3$$

If we add a solution of sodium hydroxide to an ammonium salt, ammonia is produced, especially on warming. This is owing to the fact that ammonium hydroxide is so unstable.

$$\begin{aligned} NH_4Cl + NaOH &= NaCl + NH_4OH \\ &= NaCl + NH_3 + H_2O \end{aligned}$$

Caustic soda is largely used in a number of industries, and particularly in the manufacture of soap.

Sodium Carbonate, Na_2CO_3, is manufactured on a large scale by what is known as the Solvay or Ammonia-Soda process. This depends on the fact that if a solution of ammonium bicarbonate is added to strong brine, sodium bicarbonate separates out:—

$$NH_4HCO_3 + NaCl \rightleftarrows NH_4Cl + NaHCO_3$$

The arrows indicate that the process is reversible, but by carefully regulating the conditions (especially temperature) about two-thirds of the sodium chloride undergoes the desired change.

Ammonium bicarbonate is not actually used in practice, ammonia, carbon dioxide and water being used instead ($NH_3 + H_2O + CO_2 = NH_4HCO_3$).[1] Thus the complete equation may be written

$$NH_3 + H_2O + CO_2 + NaCl \rightleftarrows NH_4Cl + NaHCO_3$$

Once sodium bicarbonate has been obtained, it has only to be heated in order to turn it into the carbonate:—

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

We must now consider the main outlines of the actual manufacturing process.

Brine obtained from the salt deposits below the ground (p. 237) is first treated with sodium carbonate, to precipitate the calcium and magnesium salts which are present as impurities in natural salt. The chemical change is the same as that which takes place in removing permanent hardness, e.g.

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[1] For full details of a laboratory illustration, see pp. 185–7 of the author's *School Course of Practical Chemistry* (Bell).

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$$

After the insoluble carbonates have settled out, the clear brine is pumped off and saturated with ammonia. It then enters a 'Solvay tower,' which is about 80 feet high, 6 feet wide and is furnished at intervals of a yard or so with grids which prevent the brine moving downwards too fast. Carbon dioxide is pumped in from below and reacts with the ammoniated brine (chiefly at the grids) in accordance with the equation already given.

One or two further points are worth considering. Notice the construction of the grids—very like the rose of a watering can. They are, however, slotted round the circumference (see fig. 36/2), and the bicarbonate, formed on the curved surface, slides to this outer rim and finds its way through the slots to the bottom of the tower. It collects there as a sort of white mud, and is pumped off to vacuum filters.

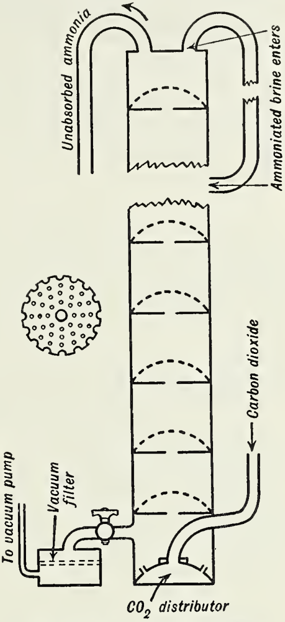

FIG. 36/2. Solvay process

Part of the carbon dioxide required is produced in specially constructed lime-kilns ($CaCO_3 = CaO + CO_2$). The remaining part is obtained in the process of turning the sodium bicarbonate into carbonate (equation already given).

From the ammonium chloride produced in the main process, ammonia is recovered by heating with slaked lime:—

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2H_2O + 2NH_3$$

The source of the slaked lime will be sufficiently obvious.

A little ammonia tends to escape unabsorbed at the top of the tower, but this is made to pass through brine, which at a later stage will enter the Solvay tower. The actual wastage of ammonia is much less than 1 per cent. In fact, the whole process is a beautiful example of chemical economy, the only waste product being calcium chloride, for which there is only a limited demand.

The sodium carbonate obtained by heating the bicarbonate consists of a fine white powder, and is known as *soda ash.* On dissolving this in hot water and crystallising out, *washing soda*, $Na_2CO_3 \cdot 10H_2O$ (often known as *soda crystals*), is obtained.

If exposed to a dry atmosphere, washing soda loses most of its water of crystallisation, the glassy crystals becoming covered with a white powder having the composition $Na_2CO_3 \cdot H_2O$. It has already been explained (p. 105) that such a change is known as *efflorescence.* The action of heat and of acids on sodium carbonate has been discussed previously (p. 178), and so has the reaction between sodium carbonate and slaked lime (p. 416).

Sodium carbonate finds a use in most homes as a cleansing agent. It is also largely used in the manufacture of glass and in several other industries.

Sodium Bicarbonate (sometimes called 'acid sodium carbonate'). This is manufactured by the action of carbon dioxide on the carbonate:—

$$Na_2CO_3 + H_2O + CO_2 = 2NaHCO_3$$

Thus in the Solvay process (p. 418) we have (i) bicarbonate made, (ii) bicarbonate heated to make carbonate, (iii) carbonate reconverted into bicarbonate. One reason for this roundabout procedure (there are several) is that the bicarbonate first produced smells of ammonia, and for many purposes this would be objectionable.

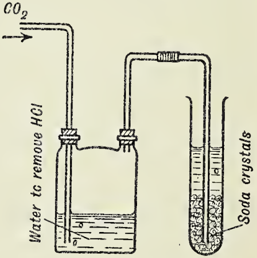

Fig. 36/3. Preparation of sodium bicarbonate

To illustrate the production of bicarbonate from carbonate, a wide test-tube is about half-filled with soda crystals ($Na_2CO_3 \cdot 10H_2O$), which are then rather more than covered with water and thoroughly shaken. This gives a saturated (or nearly saturated) solution with considerable excess of the crystals. Apparatus for the production of carbon dioxide is now fitted up (fig. 16/1). The gas is washed with water to remove hydrochloric acid, and then it is passed through the soda solution. After about three-quarters of an hour the latter becomes very milky owing to the separation of fine crystals of the bicarbonate. The gas is passed for some time longer—the longer the better—and the creamy liquid is then poured through a filter, any unchanged carbonate crystals being left at the bottom of the test-tube. The sodium bicarbonate on the filter is washed with a little water, and then transferred to a porous tile to drain and dry.

A solution of sodium bicarbonate is slightly alkaline to litmus. It does not injure the skin and can even be squirted into the eye without injurious effect. A wash-bottle of this solution is therefore often kept handy in the laboratory in case anyone should be splashed with acid.

When heated or when acted upon by acids, sodium bicarbonate gives off carbon dioxide. These reactions have already been discussed at some length on p. 179.

On p. 298 we discussed the term *basicity of an acid*, and we saw that sulphuric acid is *di*basic because it can give rise to two (and only two) distinct sulphates of the same metal (e.g. sodium sulphate, Na_2SO_4, and sodium bisulphate, $NaHSO_4$). We see now that carbonic acid is also dibasic, the derived sodium salts in this case being sodium carbonate, Na_2CO_3, and sodium bicarbonate, $NaHCO_3$.

Sodium bicarbonate is much used in the home as 'baking soda' or 'cooking soda,' and it is an important constituent of baking powder (p. 364).

Sodium is much too high in the electrochemical series to be obtained by any of the usual smelting processes. It was formerly obtained by electrolysis of the *fused* hydroxide, NaOH, sodium and hydrogen appearing at the anode and oxygen at the cathode. However, as sodium hydroxide is itself made from the chloride (p. 416) it seems much better to prepare sodium directly from the chloride than to use the hydroxide. One of many practical difficulties is the fact that sodium chloride has such a high melting-point (about 800°). This has been largely overcome by mixing with it other salts which bring down the melting-point to about 600° without themselves undergoing electrolysis.

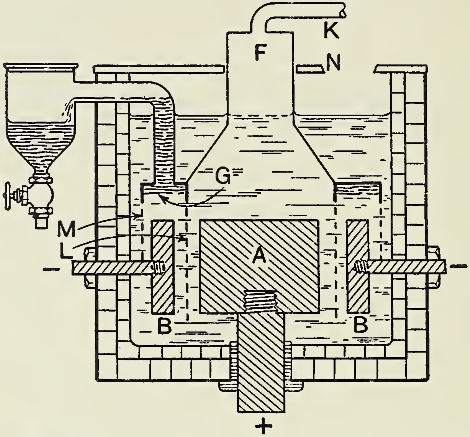

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Fig. 36/4. Sodium from sodium chloride

After its inventor the arrangement is known as the *Downes Cell*, illustrated in fig. 36/4. To withstand the high temperature the steel container is lined with refractory brick. The salt is introduced at N. The anode A is of graphite (not attacked by chlorine). B is an iron cathode. Chlorine, a valuable by-product, collects in the dome F and is piped off through K. The fused salt is kept at such a level that its pressure drives the liberated sodium up the annular space G, whence it flows into the collector. The metal screens, L, M, serve to prevent the sodium and chlorine from making contact with one another.

Sodium is a soft metal—easily cut with a knife—and so light that it will float on water. When freshly cut it is bright like silver, but in two or three seconds it tarnishes, forming the monoxide, Na_2O. This reacts with the moisture of the air, forming the hydroxide ($Na_2O + H_2O = 2NaOH$),[1] which in turn is converted into carbonate by the action of atmospheric CO_2 ($2NaOH + CO_2 = Na_2CO_3 + H_2O$). The reaction of sodium with water has already been discussed (p. 93).

Owing to the fact that it combines so readily with oxygen, sodium is usually kept under some liquid which does not contain that element (e.g. paraffin oil or petrol, both of which are mixtures of hydrocarbons).

Large amounts of sodium are used for making sodium cyanide, and even more in the manufacture of tetraethyl lead $Pb(C_2H_5)_4$, the 'antiknock' compound mentioned on p. 264. To make it, a lead–sodium alloy is first prepared from the two metals, and this is treated with ethyl chloride:—

$$4PbNa + 4C_2H_5Cl = Pb(C_2H_5)_4 + 4NaCl + 3Pb$$

The '3Pb' is used for making further supplies of alloy.

Sodium Nitrate, $NaNO_3$, has been described elsewhere (p. 332).

Sodium Nitrite, $NaNO_2$, may be produced by strongly heating the nitrate alone ($2NaNO_3 = 2NaNO_2 + O_2$). It is much more readily obtained, however, by heating it with lead, when a vigorous action takes place ($NaNO_3 + Pb = PbO + NaNO_2$). The soluble nitrite is easily separated from the insoluble lead oxide. Its chief use is in connection with the manufacture of dyes.

Sodium nitrite (or any other nitrite) is easily distinguished from a nitrate by the fact that brown fumes are produced when a dilute acid is added. No doubt nitrous acid is first produced, which rapidly decomposes into a mixture of nitric and nitrous oxides ($2HNO_2 = H_2O + NO + NO_2$). A solution of sodium nitrite, mixed with one of ammonium chloride, is sometimes used for the preparation of nitrogen:—

$$NaNO_2 + NH_4Cl = NaCl + 2H_2O + N_2$$

The gas is readily evolved on heating.

---

[1] The hydroxide is also formed *directly* by the action of atmospheric moisture on sodium, for if a piece of the metal is exposed to the air it is soon seen to be covered with small bubbles of gas (no doubt hydrogen).

Test for Sodium Compounds. Sodium compounds are easily recognised by the flame test. A porcelain rod, or platinum wire, is dipped into a small quantity of the compound which has been moistened with hydrochloric acid.[1] On holding the rod in the non-luminous bunsen flame the latter is coloured an intense golden yellow. (*N.B.* Avoid saying that 'sodium compounds burn with a yellow flame.' It is not a case of burning, i.e. of combining with oxygen, but of volatilising or turning into a vapour.)

POTASSIUM AND COMPOUNDS

On p. 261 something was said about *families* of elements, with special reference to the halogen family consisting of chlorine, bromine and iodine. Sodium is also one of a family —a family of five known as the 'alkali metals.' Another member of the family, called *potassium,* is so important that we must give some account of it here. Fortunately, potassium resembles sodium so closely that most of what we have already learnt about the one element will apply to the other.

To begin with the metal itself. It was first isolated in 1807 by Sir Humphry Davy, by the electrolysis of fused caustic potash (KOH). He had been at work on the subject for many months, and when the silvery globules of potassium made their appearance 'he could not contain his joy; he literally bounded about the room in ecstatic delight; and some little time was required for him to compose himself sufficiently to continue his experiment.'

Potassium is a soft metal, so light that like sodium it floats on water. It is even higher than sodium in the electrochemical series, so while sodium decomposes water with great energy and rusts very quickly, potassium surpasses it in both these respects.

After sodium has acted upon water, the hydroxide ($NaOH$) remains in solution. The result with potassium is similar, the hydroxide in this case having the formula KOH. We have already noted that while the hydroxides of most metals are either insoluble in water or only slightly soluble, those of both sodium and potassium are extremely soluble. The solutions feel soapy, and are strongly alkaline to litmus.

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[1] The hydrochloric acid is hardly necessary in the case of sodium compounds, but it greatly assists in many other flame tests. In most cases it causes a certain amount of *chloride* to be formed, and a chloride is a suitable compound for a flame test because it is easily volatilised.

Carbonates are usually decomposed by heat, carbon dioxide being evolved and the oxide of the metal remaining behind. Thus with calcium carbonate:—

$$CaCO_3 = CaO + CO_2$$

Here again sodium and potassium stand apart. Their carbonates are not decomposed even when heated in the electric furnace.

Let us next glance at the bicarbonates, $NaHCO_3$ and $KHCO_3$. The unusual feature here is that *these bicarbonates are sufficiently stable to exist in the solid condition.* Other bicarbonates are so unstable that they exist only in solution. Calcium bicarbonate (p. 178) is an example, and many metals are unable to form a bicarbonate even in solution.

We have seen that even sodium bicarbonate is not *very* stable—it decomposes readily enough when heated—and potassium bicarbonate resembles it in this respect.

$$2KHCO_3 = K_2CO_3 + H_2O + CO_2$$

We might notice here that because it is much more soluble than sodium bicarbonate, potassium bicarbonate cannot be prepared by a process similar to the Solvay process. This greater solubility is probably related to the higher position of potassium in the electrochemical series (cf. (6) on p. 393).

Another peculiarity of sodium and potassium we have already met with (p. 340). It is that their nitrates when heated decompose leaving *nitrites*:—

$$2KNO_3 = 2KNO_2 + O_2$$

Most other nitrates decompose in such a way as to leave *oxides*, e.g.

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$

Some further information about potassium nitrate will be found on pp. 340–1.

Potassium Chlorate has already been described (p. 256).

Test for Potassium Compounds. Potassium compounds may be recognised by means of the flame test. This is carried out as already described for sodium, but in the case of potassium compounds the flame has the colour of a lilac flower.

CALCIUM AND COMPOUNDS

When we were studying carbon dioxide and hard water we learnt quite a lot about some compounds of calcium. This will be a convenient point at which to revise our existing knowledge and to fill in the gaps.

Calcium is found in Nature mainly as the carbonate, $CaCO_3$. Chalk, limestone and marble, though differing from one another in many of their physical properties, are all varieties of calcium carbonate, both limestone and marble having been formed from chalk.

Chalk is found in great masses in the south and east of England, the cliffs of Dover being particularly well known. These deposits were originally formed in the sea. Tiny organisms lived and died there, and their hard parts—sometimes skeleton, sometimes shell—formed the material which was later hardened into chalk, and by upheaval of the sea-bed became part of the dry land. Examination of the sea-bottom shows that chalk-formation is still going on.

In much the same way *coral* has been formed in tropical seas from the skeletons of the coral polyp. A very famous example is the Great Barrier Reef off the north-eastern coast of Australia. It is no less than 1250 miles long.

Another very interesting form of calcium carbonate is *calcite* or *Iceland spar*. This consists of transparent rhombic crystals which show the peculiarity known as 'double refraction,' so that a mark on paper is seen double when viewed through this substance. Its name is due to the fact that it was first found in Iceland, and the best specimens are still obtained in that country from a small quarry which has been worked for nearly 300 years. Crystals as much as a yard across have been taken from it. Iceland spar is used in the construction of certain optical instruments.

So far we have mentioned only the occurrence of calcium carbonate in the mass, but we must note further that it is an important constituent of all fertile soils and that it forms the chief part of the shells of eggs and shell-fish (e.g. oysters), and of the skeletons of many marine organisms besides the coral polyp. Altogether it is an extremely widespread and important substance.

Calcium carbonate, like most other carbonates, is decomposed when heated. Calcium oxide (quicklime) remains behind and carbon dioxide is evolved.

$$\mathrm{Ca\quad C\quad O_3 = Ca\quad O + C\quad O_2}$$
$$\underbrace{40+12+48}_{100}\quad \underbrace{40+16}_{56}\quad \underbrace{12+32}_{44}$$

A rather high temperature is required, and in the laboratory a muffle furnace is often employed. This reaction gives us a means of finding the amount of calcium carbonate present in a mixture, provided the other components undergo no change on heating. Some of the mixture is weighed in a crucible and strongly heated until constant weight is obtained.

Suppose wt. of mixture = 4·00 gm. and
Loss of weight (i.e. wt. of carbon dioxide) = 0·79 gm.
Let x = wt. of calcium carbonate present.
Then, by *equation*, wt. of carbonate : wt. of CO_2 = 100 : 44.
By *experiment*, wt. of carbonate : wt. of $CO_2 = x : 0{\cdot}79$,
$\therefore\ 100 : 44 = x : 0{\cdot}79$, which gives $x = 1{\cdot}80$ gm.

Thus 4·00 gm. of the mixture contains 1·80 gm. carbonate, and an easy calculation shows that the percentage = ***45·0.***

On the large scale, quicklime is manufactured by heating limestone, the process being known as *lime-burning*. It is important that after the carbon dioxide has been expelled from the limestone it should not be allowed to remain in contact with the quicklime that is left; otherwise it recombines with it to a certain extent and the work is undone.

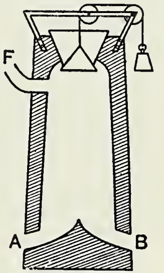

FIG. 36/5
Lime-burning
(continuous process)

A lime-kiln is constructed as shown in fig. 36/5. The limestone is broken up and mixed with about 10 per cent. of its weight of coal or coke.

The mixture is fed into the kiln through a cup-and-cone arrangement. The coke is burned, using up most of the oxygen from the air, and the nitrogen escapes through the flue F together with carbon dioxide produced from the limestone. The mixture gradually works its way down the kiln, and as fast as the limestone is raked out from below, through A and B, fresh charges are added at the top. With this type of kiln it is scarcely ever necessary to relight the fire, but, of course, the quicklime obtained is mixed with ashes. In cases where this admixture is undesirable, *either*, (i) the quicklime is separated by hand-picking, *or* (ii) the limestone is *not* mixed with coal or coke, but is heated by means of producer gas.

Calcium Bicarbonate, $Ca(HCO_3)_2$, which exists only in solution, has been dealt with elsewhere (pp. 178, 180).

Calcium Oxide, CaO (quicklime), is obtained as just described. When 'slaked' with water great heat is produced, and calcium hydroxide ('slaked lime') is formed:—

$$CaO + H_2O = Ca(OH)_2$$

Calcium Hydroxide, $Ca(OH)_2$, is only slightly soluble in water (about 1 part in 600 at ordinary temperatures). The solution is known as lime-water and is alkaline to litmus. The reaction of calcium hydroxide with carbon dioxide will be familiar.

The milky liquid obtained by shaking up calcium hydroxide with less water than will dissolve it is known as *milk of lime.* In other words, milk of lime is a *suspension* of slaked lime in water (strictly speaking, in lime-water), but do not confuse it with lime-water which has been 'turned milky' by carbon dioxide, and would be a suspension of *chalk* in water.

When heated to dull redness, slaked lime is re-converted into quicklime

$$Ca(OH)_2 = CaO + H_2O$$

Mortar is made by mixing slaked lime with about three times its weight of sand. 'Setting' is due to loss of water by evaporation. This is followed by the much slower process of 'hardening,' which consists in the gradual change of calcium hydroxide into carbonate by the action of atmospheric carbon dioxide[1]:—

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

The water produced at the same time accounts for the fact that a new house often continues to be damp for some months after being built. Sometimes this liberated moisture condenses and trickles down the walls, especially in basements. The mortar is then said to 'sweat.'

The sand serves several purposes. It helps to keep the mixture open to atmospheric carbon dioxide, and it prevents excessive shrinkage as the mortar sets and hardens. It was at one time thought that it played a small part in the hardening process by slowly reacting with calcium hydroxide and so forming calcium silicate:—

$$Ca(OH)_2 + SiO_2 = CaSiO_3 + H_2O$$

It has recently been shown, however, that this reaction does not take place at ordinary temperatures.

The gardener also has uses for slaked lime. He uses it to correct 'sourness' in soil, and to keep down slugs and other pests. He finds also that it has a curious effect on a clay soil, making it far more workable.

Calcium Chloride, $CaCl_2$, may easily be obtained by dissolving calcium carbonate in hydrochloric acid, as in the preparation of carbon dioxide, and then evaporating the residue. It eagerly absorbs moisture, forming the hydrate $CaCl_2 \cdot 6H_2O$, and on account of this property it is much used in the drying of gases. For the same reason, a solution of calcium chloride is sometimes used for 'watering' roads in hot, dry weather. A state of equilibrium is soon reached in which the chloride absorbed moisture from the air as fast as it loses it by evaporation, and the road surface remains slightly damp.

Calcium chloride cannot be used for drying ammonia, because it forms with it an unstable compound having the composition $CaCl_2 \cdot 8NH_3$.

Calcium chloride is produced on a large scale as a by-product of the Solvay process (p. 418).

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[1] An experiment illustrating the making, setting and hardening of mortar is described on pp. 201–2 of the author's *School Course of Practical Chemistry* (Bell).

Calcium Sulphate, $CaSO_4$, occurs in Nature as *anhydrite* and (combined with water of crystallisation) as *gypsum*, $CaSO_4 \cdot 2H_2O$. Owing to its very slight solubility it is easily prepared by precipitation, e.g. by adding dilute sulphuric acid to a solution of calcium chloride.

$$CaCl_2 + H_2SO_4 = CaSO_4 + 2HCl$$

If gypsum is heated to about 125° C. it loses three-quarters of its water of crystallisation and becomes *plaster of Paris* $(CaSO_4)_2 \cdot H_2O$. When the latter substance is mixed with water, heat is evolved and gypsum is re-formed:—

$$(CaSO_4)_2 \cdot H_2O + 3H_2O = 2(CaSO_4 \cdot 2H_2O)$$

The chemical change is accompanied by 'setting,' apparently because gypsum is less soluble than plaster of Paris. Let us see how this works out. Suppose a little of the plaster of Paris dissolves in the added water. It is now converted into gypsum, which being less soluble crystallises out. The process is repeated with successive quantities of plaster of Paris until the whole of it has crystallised as gypsum. The final result is that: (*a*) the added water, if suitable in amount, is all used up —i.e. the substance becomes *dry*; and (*b*) the tiny crystals, produced in a confined space, interlock with one another and form a compact mass.

When plaster of Paris sets it expands a little. This causes it to press right up to the boundaries of any cavity in which it may be placed, i.e. to take a sharp impression. Thus this substance is often used in making models; a dentist may employ it in obtaining an exact impression of a patient's mouth.

Anhydrite is now being used in large quantities in the manufacture of sulphuric acid, Portland cement (p. 385) and ammonium sulphate (p. 326).

Calcium Carbide is familiar because of its use in the preparation of acetylene (p. 197).

It is made by heating a mixture of quicklime and coke at the high temperature of the electric furnace.

$$CaO + 3C = CaC_2 + CO$$

Calcium. The metal is obtained by the electrolysis of the fused chloride. It is a very light metal (sp. gr. 1·54), rather too hard to be cut easily by a knife. It easily tarnishes in the air.

Its action on water has already been described (p. 94). This reaction is sometimes used in removing the last traces of water from alcohol. After calcium has acted upon the residual water, the alcohol is distilled off.

Test for Calcium. As in the case of sodium and potassium, the presence of calcium in a compound can be detected by means of the flame test, the colour in this case being brick-red.

Questions

N.B. *See note in italics*, p. 132

1. Describe how sodium carbonate is prepared on a large scale from sodium chloride. (No diagrams of plant are required.)

Name *three* uses for sodium carbonate and *two* for sodium bicarbonate.

Describe what happens when sodium carbonate crystals ($Na_2CO_3 \cdot 10H_2O$) are exposed to the air. *Oxf.*

2. State *very briefly* ***three*** different methods by which you could prepare in the laboratory a solution of sodium hydroxide. Give *two* commercial uses of this substance.

What would be the result of: (*a*) adding sodium hydroxide solution to a solution of ferric chloride; (*b*) passing chlorine into a cold solution of sodium hydroxide?

Give *one* use of the final solution made in (*b*). *W.J.*

3. Describe fully how you would prepare a specimen of sodium hydroxide from sodium carbonate crystals.

How is it possible to convert: (*a*) sodium carbonate into sodium bicarbonate; (*b*) sodium bicarbonate into sodium carbonate. *Camb.*

4. Describe in detail how you would prepare from caustic soda (*a*) washing soda crystals; (*b*) sodium bicarbonate. Give a simple test which would help you to distinguish between the two compounds named in (*a*) and (*b*).

State one everyday use for each of these two compounds and explain why they are used for the purpose. *W.J.*

5. A solution of sodium carbonate containing 20 gm. of anhydrous carbonate and 100 gm. of water is treated with a slow current of carbon dioxide gas until no further action takes place. Write an equation for the reaction which occurs.

Calculate the quantity of sodium hydrogen carbonate which will be precipitated from solution during the passage of the gas, given the solubility of the hydrogen carbonate at the temperature of the experiment is 9 gm. in 100 gm. of water. *O.C.*

6. Given a piece of sodium about the size of a pea, state clearly how you would safely prepare from it first a dilute solution of sodium hydroxide, and then, from this, a sample of pure common salt.

Outline the most interesting properties, both physical and chemical, of metallic sodium. *Lond.*

7. A white crystalline substance is found to give a strong yellow colour in the bunsen flame. When strongly heated, it melts and gives off oxygen. The residue is allowed to cool and is then treated with dilute sulphuric acid. The result is a vigorous effervescence, and brown fumes are given off. What was the original substance? Give equations for the chemical changes described.

8. Given sal-ammoniac (ammonium chloride), sodium nitrite, and any other chemicals you require, how would you prepare and collect jars of: (*a*) pure dry ammonia; (*b*) dry hydrogen chloride; (*c*) nitrogen? It will be sufficient to draw labelled diagrams of the apparatus in each preparation and to give the equations for the reactions which occur. *Lond.*

9. Give *two* tests by which you would distinguish between sodium bicarbonate and potassium carbonate.

10. Name *three* naturally occurring forms of calcium carbonate.

From marble chippings how would you obtain specimens of: (*a*) quicklime; (*b*) anhydrous calcium chloride; (*c*) calcium sulphate?

From pieces of quicklime how would you prepare: (*d*) slaked lime; (*e*) milk of lime; (*f*) lime-water? *Lond.*

11. 5 gm. of a mixture of calcium carbonate and quicklime was strongly heated till the weight was constant. This weight was 3·68 gm. Find the percentage of calcium carbonate in the mixture.

12. What volume of dry carbon dioxide would be obtained by heating 8·4 gm. of sodium bicarbonate to constant weight, the gas being measured (*a*) at N.T.P., (*b*) at 15° C. and 75·4 cm. pressure?

CHAPTER 37

ALUMINIUM, IRON, ZINC

ALUMINIUM

Occurrence and Extraction. Aluminium is never found free in Nature, but in combination it is the most abundant element in the earth's crust and is widely distributed. Ordinary clay, for instance, consists largely of aluminium silicate. The ore from which the metal is extracted, however, is *bauxite,* a mixture of oxides, of which the chief constituent is hydrated aluminium oxide, $Al_2O_3{\cdot}2H_2O$.

The bauxite is first carefully purified, because the quality of the aluminium finally obtained may be adversely affected by the presence of other elements, especially iron. The purification depends on the fact that while oxides of iron, etc., are insoluble in caustic soda solution, aluminium oxide ('alumina') is soluble, with the formation of sodium aluminate, $Na_2O{\cdot}Al_2O_3$:—

$$Al_2O_3 + 2NaOH = Na_2O{\cdot}Al_2O_3 + H_2O \text{ (cf. p. 152)}$$

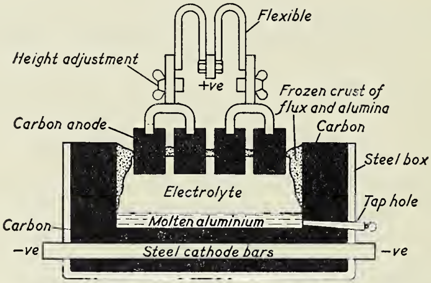
Alumina *has* been electrolysed by first melting it and then introducing electrodes, etc., but as it melts only at 2050° C., i.e. well above the melting-point of wrought iron, such a process would be quite impracticable on an industrial scale.

In Greenland, however—and nowhere else so far—there is found a mineral called *cryolite,* a double fluoride of sodium and aluminium with the formula $AlF_3.3NaF$ (or Na_3AlF_6). Now a mixture of cryolite and aluminium melts at about 900° C. Here we have a quite manageable temperature, and the electrolysis proceeds just as though only the alumina were undergoing change; so that except to make up for a little wastage, there is no need to replenish the cryolite.

Cryolite is often prepared synthetically, but the manufacturer prefers the natural material when he can get it.

The electrolysis is carried out in a steel vessel or 'cell' lined with blocks of carbon, cemented together with a carbon paste.

The carbon lining of the base forms the cathode, and to secure good electrical contact steel bars pass through it, secured with a filling of conducting carbon paste. The molten cryolite, at 970° C., is covered with a crust consisting of frozen electrolyte to which alumina has been added. From time to time part of this crust is broken in and stirred into the bath, fresh alumina being added to form a new crust.



By courtesy of Aluminium Development Association Ltd
(diagram slightly modified)

FIG. 37/1

The molten aluminium may be tapped off periodically as indicated in the figure, but in the modern furnace it is usually removed by a syphoning arrangement. Such furnaces may consist of 100 cells or so, connected in series, with a current of 40,000 amps. and a voltage drop of about 5 volts per cell. The passing of the current keeps the electrolyte in a state of fusion. The production of a ton of aluminium requires 18,000–20,000 units (kilowatt-hours)—enough to keep a two-bar electric fire going day and night for a year.

The position of the anodes is adjusted so that their lower ends are about 2–3 inches from the surface of the molten aluminium. As they are constantly in contact with oxygen at a high temperature they are steadily burnt away and have to be replaced. In fact, for every ton of metal produced, nearly two-thirds that weight of anodes is consumed.

The introduction of what is called the *Soderberg anode* is bringing about a great reduction in costs. A suitable paste

(65 per cent. ground coke and 35 per cent. pitch-tar binder) is fed at intervals into an overhead container with a square opening in the bottom. The paste makes its way through this, and at the existing temperature a baking process sets in which is complete by the time the mixture reaches the working face. Thus in effect we have a never-ending anode, made on the spot. The current enters it through steel stubs, which are raised as the lower end of the anode is consumed. In furnaces of this type currents of as much as 100,000 amps. are now being employed.

By courtesy of Aluminium Development Association Ltd

Aluminium works, Kinlochleven

In Great Britain the manufacture is carried out in certain parts of Scotland where there is plenty of water-power for the cheap production of electricity. The 'Kinlochleven' illustration reminds us of their dependence on water-power.

It is interesting to recall that the 'Hall–Héroult' process for obtaining aluminium by electrolysis was discovered in 1886 by Hall in America and Héroult in France, working quite independently. At this time both were young men, aged twenty-two, and both died in the same year, 1914.

Properties and Uses. Very pure aluminium (99·99 per cent.) resembles silver in appearances and is almost as soft as lead. The metal as usually seen, however, contains from 0·2 to 1 per cent. of impurity (chiefly silicon and iron), has a slightly bluish colour and is fairly hard. It is very malleable and ductile. One of its most striking properties is its low density, 2·7, roughly only a third that of iron (7·8) or copper (8·9). It melts at 660° C. Its electrical conductivity is about $\frac{3}{5}$ths that of copper, but because of its low density, an aluminium wire is only about half as heavy as a copper wire of equal conducting power. Aluminium is also a very good conductor of heat.

You must have noticed that an aluminium saucepan or kettle never seems to *rust* (though aluminium rust or oxide would be white, not brown). Here, appearances are deceptive. When exposed to moist air, aluminium very quickly becomes coated with an extremely thin invisible layer of its oxide, Al_2O_3. The coating is only about half of a millionth of an inch thick, but it adheres very firmly and protects the metal beneath from further oxidation, just as though that metal were coated with a perfect varnish. It is the rapid production of this coating which makes it so difficult to *solder* aluminium, because for this process the solder must make contact with the metal—not with its oxide.

For most purposes, however, the presence of the film of oxide is an advantage, for it greatly increases the resistance of aluminium to chemical action. Hence the metal is much used for containers in the chemical and food industries. Aluminium tanks used for acetic acid and for milk are two examples.

We may mention here that by making aluminium the anode of an electrolytic cell, so that oxygen is released in contact with it, we can obtain a very tough adherent coating several thousand times as thick as would be produced by the 'natural' oxidation already mentioned, thus securing even better protection for the metal beneath. The coating produced by this 'anodic' oxidation takes certain dyes remarkably well, and very decorative effects may be produced, which are nearly permanent.

It is important to notice that aluminium forms a number of alloys with one or more of the elements copper, magnesium, silicon and a few others. Generally speaking, we find that in an aluminium alloy some particular property is improved—hardness, for instance, or tensile strength—while the original properties of lightness, resistance to corrosion, etc., are not seriously affected.

We must now consider the practical uses to which we can put a metal such as we have described. These are very numerous, but limited space will allow us to deal with only a few.

To begin with, because of its lightness and good electrical conductivity, aluminium is used for nearly 90 per cent. of the overhead cable of the national grid, a core of galvanised steel wire being employed in this case to give added strength.

Its good thermal conductivity causes it to be much used in the 'heat exchangers' that are such a feature of modern manufacturing processes (cf. p. 326). In this connection no doubt we think—and quite rightly—of aluminium kettles, saucepans, etc., but actually only some 5 per cent. of the world output of aluminium is employed in this way.

Often it is not a single property, but a number of properties, that makes aluminium (or one of its alloys) suitable for a given purpose. Thus a builder would have in mind its resistance to corrosion, its lightness (reducing labour costs), good appearance and suitability for prefabrication. It is interesting to note that in this country hundreds of aluminium schools have been supplied to education authorities.

Further, aluminium plays a predominant part in the vast and expanding aircraft industry. Here, of course, regard must be paid to toughness as well as lightness, and an alloy containing copper, magnesium, manganese and silicon, after suitable 'heat treatment' (a sort of tempering process) has been found to give excellent results. Unfortunately such an alloy (containing copper) is rather easily corroded, especially where there is much contact with sea-water (e.g. carrier-based aircraft). The difficulty is surmounted by giving it a thin coating of very pure aluminium, the coated alloy being known as *alclad*.

So far, except to mention its resistance to corrosion, we have not said much about the *chemical* properties of aluminium.

It dissolves readily in hydrochloric acid, hydrogen being evolved:—

$$2Al + 6HCl = 2AlCl_3 + 3H_2$$

Hydrogen is also evolved when the metal is heated with a solution of sodium hydroxide:—

$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2$$

We may write $2NaAlO_2$ as $Na_2O \cdot Al_2O_3$. Comparing this with $Na_2O \cdot SO_3$, we see that Al_2O_3 is playing the part of an *acidic oxide* or *anhydride*, and just as $Na_2O \cdot SO_3 (= Na_2SO_4)$ is sodium sulphate, so $Na_2O \cdot Al_2O_3$ $(= 2NaAlO_2)$ is sodium aluminate.

We shall presently meet with aluminium sulphate, $Al_2(SO_4)_3$ or $Al_2O_3 \cdot 3SO_3$. Here Al_2O_3 is playing the part of a *basic oxide*. An oxide which can be either basic or acidic is said to be *amphoteric* (p. 152).

It is because aluminium (or its protecting oxide) may be dissolved as sodium aluminate that we do not use soda in cleaning aluminium pans.

We may, however, make use of this reaction to clean tarnished silver. We dissolve a handful of washing soda in boiling water, using a small enamelled bowl or other suitable container. We then put in some aluminium foil (e.g. milk-bottle covers) and touch them with the tarnished spoon or other article. The 'tarnish,' consisting of silver sulphide, Ag_2S, is quickly reduced to silver.

$$2Al + 2Na_2CO_3 + 4H_2O = 2NaHCO_3 + 2NaAlO_2 + 6H$$
$$Ag_2S + 2H = H_2S + 2Ag$$

(6H and 2H rather than $3H_2$ and H_2, because it is most likely that *nascent* hydrogen (p. 115) is concerned.)

At high temperatures aluminium shows a great affinity for oxygen. Thus, if a mixture of ferric oxide and aluminium powder is ignited, the aluminium takes oxygen from the ferric oxide and reduces it to iron:—

$$2Al + Fe_2O_3 = Al_2O_3 + 2Fe$$

The mixture is conveniently ignited by lighting a piece of magnesium ribbon which terminates in a little pile of barium peroxide mixed with magnesium filings as shown in fig. 37/2. The experiment should be carried out in a fireclay crucible. The heat produced is so intense that the iron produced is actually melted.

This reaction has received a number of useful applications. A piece of apparatus has been devised in which the molten iron can be run out of the bottom of a crucible on to any given spot—a crack in a steel propeller, for instance. The metal on each side of the crack melts, runs together, and hardens, and the crack is thus sealed up. Joints between car-lines may be sealed up in the same way. The process has been patented, and is known as the 'Thermit process.'

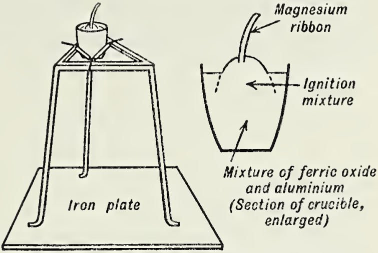

Magnesium ribbon
Ignition mixture
Mixture of ferric oxide and aluminium (Section of crucible, enlarged)
Iron plate

FIG. 37/2. Reduction of ferric oxide by aluminium.

At high temperatures aluminium combines with nitrogen, forming a *nitride*, AlN, and it is because of this property that manufacturers of steel and some other metals often add small amounts of aluminium. For steel and other metals are very apt to contain bubbles of air, and though the oxygen disappears by combination with the metal, the nitrogen remains, forming 'blowholes', which are a source of weakness. The addition of aluminium causes the removal of this nitrogen as nitride.

When we remember the many new uses that are constantly being found for aluminium and its alloys, it is not surprising to find that the output of the metal is advancing by leaps and bounds. From practically nothing at all in 1890, it had risen to 7000 tons in 1900, to 64,000 tons in 1913, and approached 3 million tons in 1955.

Important Compounds

The oxide alumina, Al_2O_3, occurs native as *corundum*. This is sometimes coloured by the presence of traces of other oxides, giving rise to various gems—the ruby, topaz, sapphire and emerald. A number of these are now made artificially by fusing alumina in the oxy-hydrogen flame and adding the necessary colouring oxide. Thus, by adding chromium oxide, artificial rubies have been produced which it is nearly impossible to distinguish from the natural article.

Corundum is nearly as hard as diamond. An impure variety of it, known as *emery*, is much used in grinding and polishing.

The hydrated oxide, $Al_2O_3 \cdot 2H_2O$, present in bauxite, has already been mentioned, and is of very great importance as the source of our supplies of aluminium.

Aluminium Sulphate is made on a large scale by the action of dilute sulphuric acid on alumina (from bauxite):—

$$Al_2O_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2O$$

It is used for the purification of water which has become contaminated with sewage.

The latter consists largely of *colloidal* material, i.e. the particles composing it, though much larger than molecules, are much too small to 'settle', or to be stopped by a filter-paper. A liquid containing such particles is often referred to as a *colloidal suspension* or *dispersion* (sometimes as a *colloidal solution*, but it is not a true solution). The particles are electrically charged, usually (as in the present 'sewage' case) negatively, and the 'like' charges on the particles cause them to repel one another. Thus they cannot run together to form particles large enough to settle out.

The addition of aluminium sulphate provides ions with a *positive* charge, Al^{+++}. These discharge the colloidal particles of sewage, which are now able to join together into particles large enough to settle. As they do so they carry with them the associated bacteria. The aluminium ion is specially effective because it carries *three* positive units of electric charge corresponding to its valency (p. 396).

Alum. Alum is a double sulphate of aluminium and potassium, having the formula $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$. One of its many uses is that it serves as a *mordant* in dyeing, i.e. a substance which enables the dye to adhere firmly to the fabric (wool, cotton, etc.). It is also used in a process for making cotton non-inflammable. When we heat a fabric which has been so treated, the contained alum soon melts (its melting-point is 92° C.), and the molten substance then forms a protecting layer over the surface of the fabric.

A solution of alum is often employed in photography for hardening the gelatine film.

We have seen that alum soon melts when heated. It also loses its water of crystallisation, and the product, *burnt alum*, is sometimes used to stop bleeding from small cuts.

This again is a colloidal action, the colloidal particles in the blood being electrically discharged just as in the 'sewage' case already discussed. The running together of the small particles constitutes *clotting*, and it is this formation of a clot which stops the bleeding. (Cf. the curdling of milk, which is a colloidal dispersion of particles of fat in water.)

IRON

Occurrence. We may notice at the outset that iron, like most other metals, is seldom found in Nature in the free or uncombined condition. It is very easy to see why. Judging by the material thrown out by volcanoes, there is plenty of free sulphur not far below the earth's surface, while in contact with the surface there is, of course, the oxygen of the air. Thus a metal is pretty certain to be turned either into sulphide or oxide, the oxide often becoming a carbonate by combining with atmospheric carbon dioxide. It is evident, then, that apart from quite special circumstances, the only metals likely to be found free, are such as do not readily form either sulphide or oxide. Gold is an example.

Iron is found in Nature chiefly as *hœmatite*, Fe_2O_3, *magnetite*, Fe_3O_4 and *iron pyrites*, FeS_2. In our own country the commonest ore is *siderite*, $FeCO_3$. As usually found this is mixed with much clay, etc., so that unfortunately its iron content is very low, about 20–30 per cent. Thus while in 1955 we used 16½ million tons of our own ore against 12 million tons imported, we obtained nearly 50 per cent. more iron from this smaller amount of imported ore than we did from that obtained at home.

The smelting process is carried out in a blast furnace, which is practically a vertical steel cylinder lined with protecting firebrick. The height may vary from 80 to 100 feet, and the diameter of the hearth from 18 to 28 feet. The charge, consisting of a mixture of iron ore, limestone and coke, is introduced into the top of the furnace by means of the double 'bell' arrangement shown. This is a device for securing that no gases escape from the furnace when a fresh charge is admitted—the upper bell automatically closes when the lower one opens.

A blast of air, previously heated, enters the furnace near its base through pipes called *tuyères,* branching off at intervals of 4 or 5 feet from the surrounding *bustle pipe.* Here we have the hottest part of the furnace, and as the blast of hot air meets the coke, carbon monoxide is formed. At such a high temperature (about 1900° C.) carbon dioxide is not first produced. The carbon monoxide passes upwards and reduces the iron ore to iron[1]: $Fe_2O_3 + 3CO \rightleftharpoons 3CO_2 + 2Fe$

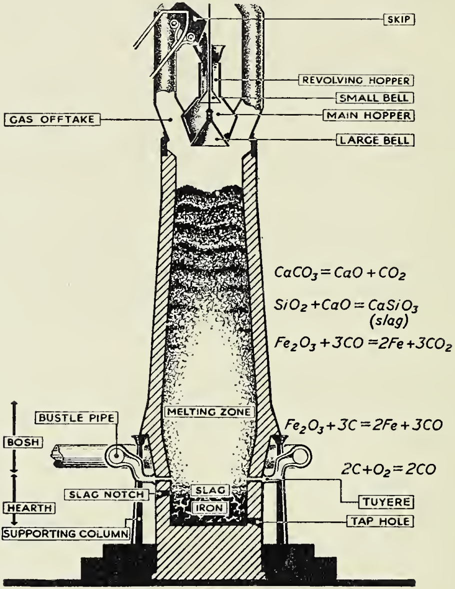


Fig. 37/3

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[1] Main diagram (slightly modified) produced by courtesy of *The British Iron and Steel Federation.* Equations are placed to indicate, roughly, the level at which the reactions occur.

Now pure iron melts at 1535° C., so in the upper part of the furnace, where the temperature is not so high, it would be solid. As it descends the furnace, however, the temperature rises, and, moreover, the iron gradually takes up carbon and acquires a much lower melting-point (the melting-point of a substance is usually lowered by the presence of impurity). It therefore melts and collects at the bottom of the furnace, from which it is run out from time to time.

Let us now consider the part played by the limestone. At the high temperature of the furnace this soon gives off carbon dioxide, forming calcium oxide ($CaCO_3 = CaO + CO_2$). Iron ore naturally contains a good deal of earthy material mixed with it, and much of this is *silica* (SiO_2), the oxide of the non-metal silicon. Now, just as calcium oxide readily combines with carbon dioxide, forming calcium *carbonate* ($CaO + CO_2 = CaCO_3$), so it will combine with silicon dioxide, forming calcium *silicate* ($CaO + SiO_2 = CaSiO_3$).

Thus the calcium carbonate is turned first into oxide and then into silicate. At the temperature reached in the furnace this silicate easily melts, forming *slag*, which, being much lighter than the molten iron, collects on the top of it and is run off from the 'slag notch.'

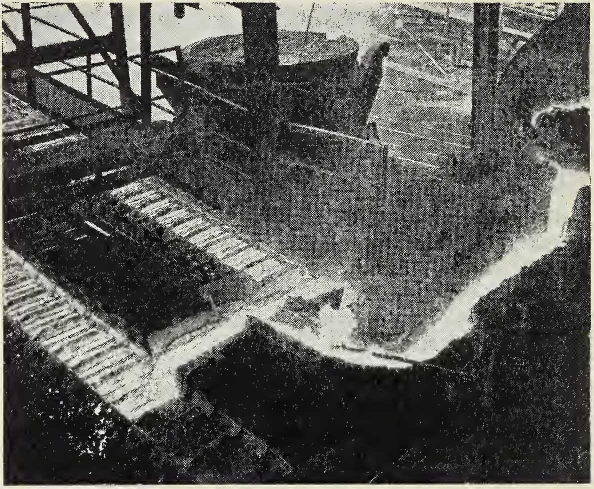
If limestone were not used, the furnace would soon be choked up with sand and clay, and would need cleaning out. By turning the sand, etc., into a fusible silicate, the furnace is practically self-cleaning, and when once set going will remain 'in blast,' as it is called, for years. Further, the molten silicate forms a protecting layer over the iron, and prevents it from being re-oxidised by the action of the hot blast.

A little way back, we spoke of the iron ore as being reduced by carbon monoxide. This happens some way up the furnace, but in the lower part, where the temperature is very high, we have reduction by carbon itself.

$$Fe_2O_3 + 3C = 2Fe + 3CO$$

The escaping gases contain about 28 per cent. of carbon monoxide. They are led through a special stove called a 'Cowper stove,' where the carbon monoxide is burnt. The heat thus produced is made to heat the air which is to be used for the blast, for it is found that if hot air is used less coke is needed in the furnace. It is worth noting that the percentage of carbon monoxide in the escaping gases is so high because the reaction between ferric oxide and carbon monoxide is *reversible*. The case is very similar to the one we discussed on p. 97.

The molten iron used to be run into troughs made in a sand-bed, but it is now run into shallow steel troughs which are carried slowly up a slight incline as a sort of endless chain (a double chain in the illustration), and which on their way to the store-shed are cooled by water. This *pig iron*, as it is called, undergoes a slight refinement in a special 'cupola' furnace (something like a small blast furnace), where it is remelted with the addition of a little scrap iron. The product is sent off to the foundries as *cast iron*. It contains 3–4 per cent. of carbon, together with small quantities of sulphur, silicon, phosphorus and manganese. When iron is dissolved in dilute sulphuric or hydrochloric acid, some of the impurities form compounds with the hydrogen. Thus the carbon gives rise to hydrocarbons (e.g. acetylene, C_2H_2), the sulphur to hydrogen sulphide, H_2S, and the phosphorus to phosphine, PH_3. It is this mixture of hydrogen compounds—and especially the



By courtesy of American Iron and Steel Institute

Pig-casting machine

last two—which is responsible for the unpleasant smell. Hydrogen itself, of course, has no smell.

Only about a fifth of the pig-iron output becomes cast iron. The rest is converted into steel.

Cast Iron, Wrought Iron and Steel. The cast iron mentioned above has a low melting-point (for iron)—about 1100° C.—and has the further property of expanding when it solidifies; hence it is very useful for making castings. For this purpose it is poured into a mould of sand, and on solidifying it pushes its way into every crevice of the mould, thus giving a 'sharp' casting.

By a special process known as 'puddling'—we shall not stop to describe it here—the carbon may be almost completely removed from cast iron, the product being known as ***wrought iron.*** This has a melting point of about 1500° C.—much higher than that of cast iron. At a red heat it is malleable, i.e. it can be beaten out with a hammer, and it is on this property that the blacksmith's work depends. Further, two red-hot pieces may be welded—beaten together and made to form one piece.

It should be mentioned that a variety of iron, in some respects intermediate between 'wrought' and 'cast', is also manufactured in large quantities. Articles are made from it by the process of casting, followed by machining to exact shape if necessary. It differs from ordinary cast iron, however, in being able to withstand considerable shock, and in fact it is often known as 'malleable cast iron.'

Wrought iron is still used for making horseshoes and the cores of electro-magnets, but for most other purposes it has been superseded by ***steel.***

Steel contains up to about 1·4 per cent. of carbon (rarely more), i.e. it contains more than wrought iron, but less than cast iron or pig iron.

To turn pig iron into steel we must therefore *reduce* the carbon content; and as a slight change in the percentage of carbon makes a great difference to the quality of the steel, it is necessary that this percentage should be known with great accuracy.

Modern methods of steel manufacture date from 1856, when Henry Bessemer invented a process in which the whole of the carbon (and other impurities) was first burnt away by blowing air through the molten pig iron. The calculated amount of carbon, usually included in a special variety of pig iron known as *spiegeleisen*, was then added.

The old-fashioned steel manufacturers treated Bessemer's process with some contempt at first, but when they found that he could produce better steel than theirs and could afford to sell it at £20 a ton cheaper, they were obliged to take serious notice of it. Soon they were paying Bessemer large sums of money for the right to use his patent—in fact, the inventor made over a million pounds out of his discovery. Later on he was knighted. He died in 1898 at the age of eighty-five.

Basic Slag. Bessemer found that one of the impurities most difficult to eliminate was phosphorus. This problem was solved in 1878 by a man named Thomas. He lined the 'converter' with *dolomite* (a double carbonate of calcium and magnesium, $CaCO_3 \cdot MgCO_3$), and a calculated quantity of lime was also added with each charge of metal. By the action of the air-blast the phosphorus present is turned into phosphorus pentoxide, an *acidic* oxide, P_2O_5. Calcium carbonate, by loss of carbon dioxide, easily becomes calcium oxide, CaO, a *basic* oxide. The basic and the acidic oxides then combine, forming calcium phosphate, $(CaO)_3 \cdot P_2O_5$ or $Ca_3(PO_4)_2$. In a similar way we have magnesium phosphate produced from the magnesium carbonate present.

This mixture of calcium and magnesium phosphates is known as ***Thomas's basic slag***, and farmers will pay a good price for it as a fertilizer.

The Open-earth Process. In Great Britain the Bessemer process has largely given place to what is called the open-hearth process. We may notice two features which are common to both.

(1) In both processes we start with molten metal direct from the blast furnace (thus greatly reducing fuel costs). The molten metal is run from the blast furnace into the 'mixer' (a large steel vessel lined with firebrick), in which it will be conveyed to the steel-works. Some of these mixers are comparatively small, but others are made to hold as much as 1000 tons of molten iron.

(2) In both we use the principle of the basic lining[1] (and added lime) already mentioned, so that the phosphorus is removed as calcium and magnesium phosphates.

The chief difference is in the method employed to oxidise the carbon and other impurities. In the Bessemer process, as we have seen, a blast of air is employed. In the open-hearth process a fierce flame of producer gas,[2] fed with excess of air, beats down on the molten metal, with which scrap iron is often mixed. The carbon, phosphorus, etc., are oxidised, partly by the excess of air, partly by hæmatite (Fe_2O_3), which is added at a later stage, and which is itself, of course, reduced to iron.

But steel contains *some* carbon, and the operator tries so to control the reaction as to leave the necessary amount unoxidised. However, near the end analyses are made, and any adjustments can be made by the addition of the calculated amount of spiegeleisen or other necessary materials.

Properties of Steel. Like wrought iron, steel can be hammered out and welded, but its most remarkable property is that it can be *hardened* and *tempered*. It is hardened by making it red-hot and then suddenly cooling it. It is then extremely brittle, and so hard that small wheels for scratching glass can be made from it. If it is now heated up to a moderate temperature (230°–330°) and cooled, the metal is much less brittle than before, and is therefore of far more general use. It is said to have been *tempered*. Its exact degree of hardness, etc., will depend on the (second) temperature to which it was heated and on the conditions under which it was cooled (e.g. slowly or quickly). Thus, by varying the treatment, different kinds of steel may be obtained—one suitable for making razor blades, another for large saws and so on. This capacity for taking a temper may be regarded as one of the general properties of steel. Another general property is that it is *malleable*, though not always at ordinary temperatures.

From what has been said, it will be clear that steel of specified properties may often be obtained simply by applying the appropriate heat treatment. We can also vary the amount of carbon. In general, the 'low carbon' steels—steels with less than 0·15 per cent. of carbon—are 'soft,' while 'high carbon' steels (0·5–1·4 per cent.) are 'hard'; and there are, of course, intermediate grades.

---

[1] A basic lining is *not* used if the pig iron is comparatively free from phosphorus, but that is not usually the case if the iron has been extracted from an ore of British origin.

[2] Sometimes oil is used, especially in America.

We must now consider the ***alloy steels.*** For simplicity we have so far spoken only of the presence of *carbon* in steel. For generations, however, it has been known that steel is improved by the presence of *manganese*, which is present in the spiegeleisen already mentioned.

Of late years other elements besides carbon and manganese have been introduced into steel, and it has been found possible to make steel having almost any desired properties. Thus ***nickel steel*** (containing about 3 per cent. of nickel and about 0·25 per cent. of carbon) is extremely hard without being brittle, and is therefore used for the armour-plating of battleships—a brittle steel would be shattered if struck by a shell.

Ordinary steel contains, in addition to carbon, a small amount of manganese—0·4 per cent. or so. ***Manganese steel,*** however, contains a much larger proportion, about 12 per cent. Its properties are somewhat similar to those of nickel steel. It is often used for the jaws of the rock-crushing machinery employed in mining, and in war-time it is used for making helmets to protect soldiers against shrapnel. Unlike ordinary steel, it retains its hardness after being heated and cooled, and so is used in making safes.

Then there is the familiar ***stainless steel,*** used not only for cutlery but in numerous other ways, e.g. in chemical works for making containers to hold nitric acid and many organic acids. This particular alloy is often known as 'eighteen–eight,' because it contains 18 per cent. of chromium and 8 per cent. of nickel.

These alloy steels are made by means of the electric furnace, the source of heat being usually an electric arc struck between large carbon electrodes serving as one pole, and the metal with which the furnace is charged as the other. In this process the temperature may be as high as 3400° C., but it can be very exactly regulated, and there are no complications due to the chemical action of fuel gases on the molten metal (such gases, of course, being absent). Thus steel of any given composition can be produced more easily than by any other process. The disadvantage is that, owing to the cost of current, it is more expensive to produce.

Compounds of Iron. Iron forms two distinct series of compounds

(i) ***Ferrous*** compounds in which the iron is divalent, e.g. ferrous oxide, FeO; ferrous chloride, $FeCl_2$; ferrous sulphate, $FeSO_4$, etc.

(ii) ***Ferric*** compounds in which it is trivalent, e.g. ferric oxide, Fe_2O_3; ferric chloride, $FeCl_3$; ferric sulphate, $Fe_2(SO_4)_3$.

Ferrous salts in the hydrated condition (i.e. with water of crystallisation) are made by dissolving iron in the appropriate acid. Ferrous sulphate, for instance, is easily made by dissolving a quantity of iron filings in dilute sulphuric acid, filtering to get rid of undissolved iron (or insoluble impurities) and then leaving to crystallise out[1] ($Fe + H_2SO_4 = FeSO_4 + H_2$). The crystals obtained have the composition $FeSO_4 \cdot 7H_2O$.

Ferric salts are easily produced by the oxidation of the corresponding ferrous compounds. Suppose, for instance, we wish to turn ferrous sulphate, $FeSO_4$, into ferric sulphate, $Fe_2(SO_4)_3$. To attain our object we must add on an 'SO_4' group to $2FeSO_4$. That would give us $Fe_2(SO_4)_3$. The obvious source of the 'SO_4' group seems to be sulphuric acid, H_2SO_4, but to liberate this group, the hydrogen must be removed—by oxidation. Thus we should have

$$2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O$$

Various oxidising agents may be used, but the best is nitric acid—*best* because the substances formed by its reduction (chiefly nitric oxide and nitrogen dioxide) are gases, and can therefore easily be expelled from the solution.

In a similar way—by heating with *hydrochloric* acid and nitric acid—we can turn ferrous chloride into ferric chloride:—

$$2FeCl_2 + 2HCl + O = 2FeCl_3 + H_2O$$

---

[1] The filtered solution should not be heated, or brown oxidation products are very likely to be formed.

We may sum up our results in the general rule: *To turn a ferrous into a ferric salt, heat with the corresponding acid together with nitric acid, the latter acting as oxidising agent.*

Sometimes a special method may be used. Thus, by simply passing chlorine into a solution of ferrous chloride we obtain ferric chloride—an example of the oxidising action of chlorine:—

$$2FeCl_2 + Cl_2 = 2FeCl_3$$

Before passing on we might notice that when we speak, for example, of ferrous sulphate, $FeSO_4$, being *oxidised* to ferric sulphate, $Fe_2(SO_4)_3$, we are strictly in line with the definition of oxidation at which we arrived on p. 279. That definition includes 'gain of oxygen or other electronegative element or group,' and as explained on the page mentioned, SO_4 is an electronegative group.

The case mentioned is just an example of the general rule, that when an element changes its valency it also changes what we may call its degree of oxidation.

Anhydrous Ferrous and Ferric Chlorides. The methods so far described apply only to the preparation of *hydrated* salts. *Anhydrous* iron salts are usually prepared by special methods. Anhydrous ferric chloride, for instance ($FeCl_3$), is made by passing dry chlorine over strongly heated iron gauze (see fig. 37/4, p. 451). If instead of chlorine we use dry hydrogen chloride,[1] anhydrous ferrous chloride, $FeCl_2$, is obtained.

Ferrous Salts from Ferric. We have just seen how to turn ferrous into ferric salts. What about the converse process, ferric to ferrous? Let us consider ferric sulphate, $Fe_2(SO_4)_3$. If we can only get rid of one 'SO_4' group our $Fe_2(SO_4)_3$ will become $2FeSO_4$. It seems as if the most promising method would be to make the SO_4 group combine with hydrogen. Now, on passing hydrogen through a solution of ferric sulphate nothing happens. If, however, the hydrogen is generated *within the solution*, say by adding zinc and dilute sulphuric acid, then reduction soon takes place. As explained on p. 115, the difference is apparently due to the fact that in the second case the hydrogen is *nascent*, while in the first it is not:—

$$Fe_2(SO_4)_3 + 2H = H_2SO_4 + 2FeSO_4$$

---

[1] A steady stream of this is conveniently obtained by putting concentrated hydrochloric acid in a flask and allowing concentrated sulphuric acid to drop into it from a dropping-funnel.

The method as described suffers from one drawback—we have introduced *zinc*, and so our solution of ferrous sulphate would be mixed with zinc sulphate. To avoid this we can use iron filings instead of zinc.

To reduce ferric chloride to ferrous chloride we could use iron and hydrochloric acid:—

$$FeCl_3 + H = FeCl_2 + HCl$$

(H = an atom of nascent hydrogen), and in fact we may generalise by saying, *to turn a ferric into a ferrous salt, add the corresponding acid and a quantity of iron.*

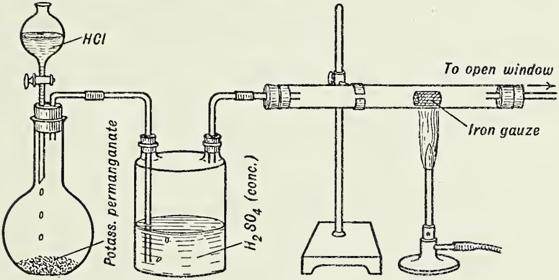


FIG. 37/4. Preparation of anhydrous ferric chloride

Distinction between Ferric and Ferrous Salts. There are many ways of finding whether an iron salt is 'ferrous' or 'ferric,' but it will suffice to give the following three:

(i) A solution of a ferrous salt has a watery-green colour, while a solution of a ferric salt is yellow or brown.

(ii) If ammonia is added to a solution of a ferrous salt, a green precipitate is obtained. In the case of a ferric salt the precipitate is brown. The precipitates consist of ferrous hydroxide,[1] $Fe(OH)_2$, and ferric hydroxide, $Fe(OH)_3$, respectively, e.g.

$$FeCl_2 + 2NH_4OH = Fe(OH)_2 + 2NH_4Cl$$
$$FeCl_3 + 3NH_4OH = Fe(OH)_3 + 3NH_4Cl$$

---

[1] This is not strictly true. Ferrous hydroxide is *white*, and this colour can be seen just for a moment. It rapidly oxidises, however, and the green precipitate is really a complex compound of ferrous hydroxide and ferric hydroxide.

(iii) On adding potassium thiocyanate (KCNS) to a solution of a ferric salt, a blood-red coloration (ferric thiocyanate) is obtained; with ferrous salts the colour does not change:—

$$FeCl_3 + 3KCNS = Fe(CNS)_3 + 3KCl$$

The last test is a very delicate one, and a ferrous salt will often show a slight pink tinge when the thiocyanate is added. This is because, owing to the oxidising action of the atmosphere, a little of the ferrous salt has been converted into ferric.

Ferrous Sulphate, $FeSO_4{\cdot}7H_2O$ ('green vitriol'), is the most important of the ferrous salts. We already know something about it—how it is prepared (p. 449), and the part it plays in the 'brown ring test' (p. 347).

When strongly heated, green vitriol undergoes changes which are approximately as follows:

(i) Water of crystallisation is given off:—

$$FeSO_4{\cdot}7H_2O = FeSO_4 + 7H_2O$$

(ii) The sulphate is decomposed:—

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$$

(iii) Water and sulphur trioxide combine, forming sulphuric acid:—

$$H_2O + SO_3 = H_2SO_4$$

Thus, by strongly heating green vitriol under such conditions as are indicated in fig. 37/5, it is possible to obtain sulphuric acid. This acid was made from green vitriol many centuries ago by the Arabs, and so received its name of ***oil of vitriol***—i.e. the oily liquid obtained by heating green vitriol.

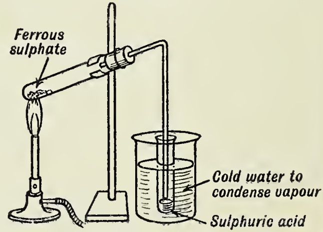


FIG. 37/5. Heating ferrous sulphate

Ferrous sulphate is used in making ink, which consists of a solution of this substance mixed with gum arabic, an organic compound called tannin and a blue dye. Ferrous tannate is formed in the solution, but this has such a pale colour that the blue dye has to be present to make the writing show. The blue dye, in fact, acts as a *temporary* ink. On exposure to air, the ferrous tannate is oxidised to ferric tannate, which is deep black.

Ferric Oxide, Fe_2O_3, is a red powder which may be prepared by many methods, of which one has just been described. When prepared in this way (i.e. by heating green vitriol) the powder is very finely divided, and is much used by jewellers for polishing silver plate, etc. ('jeweller's rouge'). It is also used in the manufacture of red paint.

Another method of preparing it consists in first precipitating the hydroxide, $Fe(OH)_3$, by adding ammonia to a solution of a ferric salt as already described. After being filtered, washed and dried, the hydroxide is then ignited (i.e. strongly heated), when the oxide is produced:—

$$2Fe(OH)_3 = Fe_2O_3 + 3H_2O$$

We have already seen that this oxide occurs in Nature as the mineral hæmatite.

Mixed with other substances, ferric oxide is very widely distributed and has been called 'the artist of Nature,' because it is so often responsible for imparting colour effects. The red colour of sandstone, for instance, is due to its presence.

Rust consists chiefly of the hydrated oxide, $2Fe_2O_3 \cdot 3H_2O$.

It is formed as the result of an electrolytic process of a rather special type. Let us go back to the simple cell of fig. 34/1 (p. 391). There zinc, the higher of the two metals in the electrochemical series, goes into solution.

Now think of a scratch on the surface of iron (much exaggerated in fig. 37/6). The dotted lines represent the surface of a film of moisture made slightly acid by solution of carbon dioxide. It has been shown experimentally that iron with plenty of oxygen (or air) near it is actually lower in the series than iron not so well supplied. Thus the iron at B is to that at A in much the same relation as the zinc plate of our cell is to the copper plate. At B, then, ions go into solution ($Fe_{metal} \rightarrow Fe^{++} + 2e$), while the liberated electrons run round to A, and with oxygen and water give hydroxide ions ($\frac{1}{2}O_2 + H_2O + 2e = 2OH^{2e}$ or $2OH^{--}$).

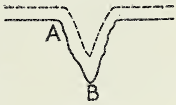


FIG. 37/6

The ferrous ions Fe^{++} diffuse outwards and soon make contact with the OH^- ions, producing ferrous hydroxide round the mouth of the scratch, and by reaction with oxygen and water this easily becomes 'rust.' At the bottom of the scratch, more iron goes into solution, and the scratch gradually enlarges to a little cave.

Ferroso-ferric Oxide (=ferrous-ferric oxide), Fe_3O_4, is so called because it may be regarded as $FeO{\cdot}Fe_2O_3$, i.e. a compound of ferrous oxide, FeO, and ferric oxide, Fe_2O_3.

We have already seen (p. 96) that this oxide is produced as a greyish-black substance when steam is passed over heated iron ($3Fe + 4H_2O = Fe_3O_4 + 4H_2$). It is also formed when iron is strongly heated in air or oxygen. Thus 'smithy scales,' struck by the blacksmith from heated iron, consist of this oxide.

When acted upon by acids it behaves as a sort of mixed base, giving rise to a mixture of ferrous and ferric salts. To obtain the equation we note that FeO would require $2HCl$ (to give $FeCl_2$) and Fe_2O_3 would take $6HCl$ (to give $2FeCl_3$). Thus $FeO{\cdot}Fe_2O_3$ would need $8HCl$, and we get

$$Fe_3O_4 + 8HCl = FeCl_2 + 2FeCl_3 + 4H_2O$$

This oxide is found native as *magnetite* or *lodestone* (=leading stone), so called because of its magnetic properties. Centuries ago men found that if a piece of the substance were suspended by a cord, its axis always set in a particular direction, and no doubt they often guided themselves over the hills and moorlands with this rude form of compass.

ZINC

Occurrence. Zinc is found chiefly as *zinc blende*, ZnS; another important ore is *calamine*, $ZnCO_3$.

Extraction. The ore is first roasted, zinc oxide being formed:—

$$[ZnS + 3O = ZnO + SO_2]$$
$$2ZnS + 3O_2 = 2ZnO + 2SO_2$$

(The sulphur dioxide is often used in the manufacture of sulphuric acid; cf. treatment of iron pyrites, p. 289.)

In the next operation advantage is taken of the facts: (i) that zinc oxide, like most other oxides, is reduced to the metal on heating with carbon; (ii) that zinc—for a metal—is *volatile*, i.e. is comparatively easily turned into a vapour. (Zinc actually *boils* at 907° C., a lower temperature than that at which cast iron *melts*.)

The oxide obtained by the roasting process already mentioned is first mixed with half its weight of powdered coal, and is then placed in a fireclay retort. A considerable number of these retorts are heated by gas in a kind of muffle furnace. As the oxide begins to be reduced, the blue flame of carbon monoxide appears at the mouth of the retort:—

$$ZnO + C = Zn + CO$$

The blue flame soon changes to a dazzling white, a sign that zinc is beginning to distil over. It is collected in clay receivers.

Some years ago a very interesting method of zinc extraction originated at Trail, British Columbia. First of all the ore is roasted as already described, and the sulphur dioxide is at once turned into sulphuric acid at works erected practically on the spot. The zinc oxide produced by the roasting process is now dissolved in the sulphuric acid, a solution of zinc sulphate being obtained:—

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

Lastly, the zinc sulphate solution is submitted to electrolysis, zinc of a very high degree of purity (99·99 per cent.) being obtained. The necessary electric current is derived from water-power.

This method has now been adopted in many other parts of the world where conditions (cheap water-power, for instance) are suitable, and at the present time (1957) accounts for about half of the world's output.

Properties and Uses. Zinc is a bluish-grey metal melting at 418° and boiling at 907° C. When quite pure it dissolves only very slowly in dilute sulphuric acid, but 'commercial zinc' dissolves readily enough. There is no doubt that in the presence of impurities an electrical action is set up (cf. the solution of zinc in a voltaic cell on closed circuit), but the full explanation belongs to Physics rather than to Chemistry. The impurity usually present is *lead*. Some of this metal (as sulphide) occurs along with the original zinc blende, and a little of it volatilises along with the zinc.

Zinc is very like copper in its behaviour with concentrated sulphuric acid, i.e. there is no action in the cold, but on heating, the acid is reduced to sulphur dioxide (cf. equation on p. 277).

Zinc is often used in the laboratory in the preparation of hydrogen (the equation has just been given). When making hydrogen by this method you have probably noticed, after the zinc has dissolved, a lot of black specks floating about in the dilute acid. These specks are the lead of which we have spoken.

Of late years the black specks have been less noticeable—and the zinc has been more difficult to dissolve. The reason in both cases is that purer zinc is being put on the market. In case of difficulty it may be necessary to add a few drops of copper sulphate solution. Zinc acts upon this, liberating copper ($Zn + CuSO_4 = ZnSO_4 + Cu$), and the copper then acts, probably, in pretty much the same way as the lead would have done.

Zinc is largely used for 'galvanising' iron, so as to protect it from rusting. Sheet iron, after being thoroughly cleaned, is dipped into a bath of molten zinc. A thin coating of the latter metal clings to it, and as it solidifies it gives the curious crystalline effect that you have seen on new buckets, etc.

It may easily happen (e.g. from a scratch) that the zinc and iron are both exposed, and when rain falls on the junction, with carbon dioxide or sulphur dioxide in solution making an acid, we have a small voltaic cell set up. In such a case it is the more electropositive metal—zinc in the present instance—which is dissolved, and the iron escapes corrosion so long as any zinc remains near it.

On the other hand, if iron is coated with tin or copper and the junction is exposed, it is the more electropositive *iron* which is attacked (cf. p. 453).

Zinc is widely used in the manufacture of the cases of dry cells, and also in the building trade (e.g. for giving a watertight junction between chimney and roof). Much zinc is also used in the manufacture of *brass* (an alloy of zinc and copper).

Zinc Sulphate. You will have come across this substance while preparing hydrogen from zinc and dilute sulphuric acid. The contents of the flask may be filtered, when the sulphate ($ZnSO_4 \cdot 7H_2O$) readily crystallises out. It is sometimes known as *white vitriol.*

When heated to 100°, six of the seven molecules of water of crystallisation are given off. To drive off the remaining molecule a dull red heat is required. We have already referred (Chap. 9, p. 105) to the fact that a salt often holds on very tenaciously to its last molecule of water of crystallisation.

When strongly heated, zinc sulphate is decomposed into zinc oxide and sulphur trioxide (cf. ferrous sulphate, p. 452):—

$$ZnSO_4 = ZnO + SO_3$$

Zinc Hydroxide, $Zn(OH)_2$, is obtained as a white precipitate when sodium hydroxide is added to a solution of a zinc salt, e.g. the sulphate:—

$$ZnSO_4 + 2NaOH = Zn(OH)_2 + Na_2SO_4$$

If we continue to add the sodium hydroxide, the white precipitate dissolves. We can understand better what has happened if we regard sodium hydroxide, NaOH, as $Na_2O \cdot H_2O$ ($=2NaOH$), and zinc hydroxide, $Zn(OH)_2$, as $ZnO \cdot H_2O$. Just as the strongly basic sodium oxide will combine with the acidic carbon dioxide to form sodium carbonate, $Na_2O \cdot CO_2$ or Na_2CO_3, so in the case before us it is combining with zinc oxide, ZnO, forming $Na_2O \cdot ZnO$ or Na_2ZnO_2 (sodium zincate). Thus the zinc oxide, usually basic as in zinc sulphate ($ZnSO_4$ or $ZnO \cdot SO_3$), is here acting as an acidic oxide. It is in fact an *amphoteric* oxide (cf. Al_2O_3 on p. 438).

Sodium zincate is also formed, with evolution of hydrogen, when zinc is heated with a solution of sodium hydroxide:—

$$Zn + 2NaOH = Na_2ZnO_2 + H_2$$

To go back to zinc hydroxide, if *very* gently heated it may be dried without decomposition, but above 85° it is decomposed into zinc oxide and water:—

$$Zn(OH)_2 = ZnO + H_2O$$

Zinc Oxide may be prepared by any of the usual methods (see Appendix, pp. 518–9).

It is used in the preparation of a white paint known as 'zinc white,' and if required for this purpose it is made by burning zinc shavings in the air, when it is formed as a bulky white powder which used to be called 'philosopher's wool.' Zinc white has not nearly the 'body' or covering power that 'white lead' possesses, but it has one great advantage. Both zinc oxide and white lead are gradually turned into the corresponding sulphides on exposure to the air of towns (because such air contains small quantities of hydrogen sulphide). Now zinc sulphide is white, like the original oxide, while lead sulphide is *black*. Hence a white lead paint soon darkens in colour. The darkening of an old oil-painting is due to the same cause. A paint containing zinc oxide would evidently undergo no change of colour.

Zinc oxide may be recognised by its curious property of turning yellow when heated. It regains its white colour on cooling.

Questions

N.B. *See note in italics*, p. 132

1. Describe how aluminium is obtained from natural sources. What are the chief uses of aluminium?

How does aluminium react with: (*a*) air; (*b*) hydrochloric acid; (*c*) aqueous sodium hydroxide? *O.C. Alt.*

2. Describe an experiment in which ferric oxide is reduced by aluminium, and mention any practical application of this reaction.

3. A certain compound, which contains 75 per cent. of aluminium and 25 per cent. of carbon by weight, is decomposed by water, forming aluminium hydroxide and methane. Calculate: (*a*) the simplest formula for the compound; (*b*) the volume of methane, at 18° C. and 750 mm. pressure, which would theoretically be set free when 10 gm. of the compound is added to water.

4. Pig iron may be made from hæmatite (Fe_2O_3) in a blast furnace. Name the other materials put into the furnace, and outline the chemical reactions in which they take part.

From iron filings how would you prepare specimens of: (*a*) ferrous sulphide, and (*b*) triferric tetroxide? Describe the effect of hydrochloric acid on these two substances. *Lond.*

5. With the help of the Index, record as many examples as you can of *reversible reactions,* and give the equations. Under what circumstances will a reversible reaction give rise to chemical equilibrium? Give an example.

Mention a case in industry in which the fact that a certain chemical reaction is reversible is a serious nuisance. What steps are taken to minimise the difficulty?

6. How would you prepare a specimen of crystalline ferrous sulphate from iron filings?

What happens when ferrous sulphate crystals are: (*a*) heated alone; (*b*) warmed with nitric acid; (*c*) dissolved in water, treated with a solution of sodium hydroxide, and the product allowed to stand in air? *Dur.*

7. Describe briefly how you would prepare anhydrous specimens of: (i) ferrous chloride; (ii) ferric chloride. *J.M.B.* (*part*)

8. How would you convert: (i) a solution of ferrous chloride into one of ferric chloride; (ii) a solution of ferric chloride into one of ferrous chloride?

9. How much iron is present in 20 gm. of crystallised ferrous sulphate, $FeSO_4{\cdot}7H_2O$? How could you obtain this iron?

10. A brown compound was found to have the following percentage composition: iron, 59·9; oxygen, 25·7; water, 14·4. Find its simplest formula. What is the compound?

11. Describe the manufacture of zinc from one of its ores. How does this metal react with: (*a*) hydrochloric acid; (*b*) caustic soda?

Mention *two* uses of zinc.

What is the effect of heat on zinc oxide? *O.C.* (*part*)

12. When strongly heated, a certain substance gave off a gas which turned lime-water milky. The residue was yellow while hot but became white on cooling. What was the original substance?

CHAPTER 38

COPPER, LEAD, MERCURY

COPPER

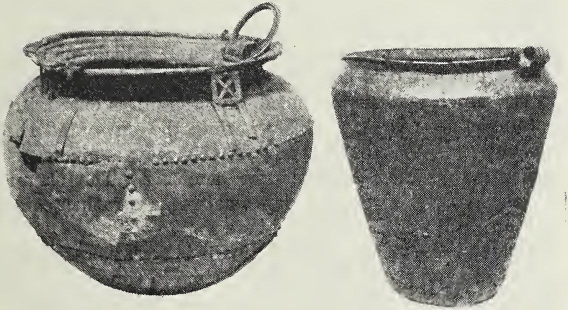
History. The use of copper coincides with one of three long chapters in the history of the human race. In the Stone Age men used tools and weapons made of flint. Later they used bronze, an alloy consisting of copper together with a little tin. The Stone Age and the Bronze Age finally gave place to the Iron Age.

By courtesy of The British Museum

Large copper relief from near Ur (*c.* 3100 B.C.)

Copper is found in the metallic condition in various parts of the world. Further, some of its ores are very easily reduced to the metal. It is not surprising, therefore, to find that copper has been in use from very ancient times, and specimens of cast copper have been found in Egypt dating from about 4000 B.C. In fact, with the exception of gold, copper was probably the first metal to be worked by man. Because of its resistance to the action of air and water, articles of very ancient date are unearthed from time to time, often in surprisingly good condition, as will be seen from the illustrations given.

It is quite possible, as already pointed out, that the primitive Egyptian industry represented on p. 384 is actually copper-smelting. The date is about 2000 B.C. The Greeks and Romans obtained their copper from the island of Cyprus, and this was called by the Romans *œs cyprium* (i.e. Cyprian brass). *Æs cyprium* was shortened to *cyprium*, which finally became *cuprum.*



By courtesy of The British Museum

Bronze cauldron and bucket (c. 700 B.C.)

It was probably by a lucky accident that some ancient coppersmith found that if a little tin were added to the copper the metal was hardened and made much more useful for all sorts of purposes. It is certain that bronze was worked as early as 2500 B.C., and possibly much earlier.

Occurrence. Although uncombined copper is fairly widely distributed, it is only to the north of Lake Superior that it occurs in considerable quantities. There, the free copper is usually present as small particles mixed up with the other ore, and no attempt is made to separate it—it goes through the normal smelting process. Occasionally, however, boulders of almost pure copper have been found. One of these weighed 420 tons!

Oxides and carbonates are found, but the commonest copper ores are sulphides, of which *copper pyrites*, $CuFeS_2$, is the most important.

Extraction. An easy calculation shows that pure copper pyrites would contain nearly 35 per cent. of copper. Actually, the ore is mixed up with so much useless earth and rock ('gangue') that the percentage is much more often in the neighbourhood of *two*!

From such poor stuff it would not pay to extract the copper directly. It is therefore first finely ground, and then submitted to the 'froth flotation' process. For this, the crushed material is placed in a tank of water and a little pine oil is added. The liquid is now violently agitated by blowing air into it. Much froth is produced, and the ore is entangled in the bubbles and is skimmed off, while the unwanted rocky particles settle to the bottom. In this way a much richer product is obtained, suitable for smelting. The chemical changes involved in present-day smelting are rather complicated, and will not be discussed here.

An older method still used in Spain is to build very large heaps of ore and sprinkle them from time to time with water. After a considerable period, by the action of air and water, the ore becomes oxidised to copper sulphate. This is washed out with water, and copper is precipitated from the solution by means of scrap iron ($CuSO_4 + Fe = FeSO_4 + Cu$).

Copper pyrites is often burnt in the manufacture of sulphuric acid, to produce the necessary sulphur dioxide:—

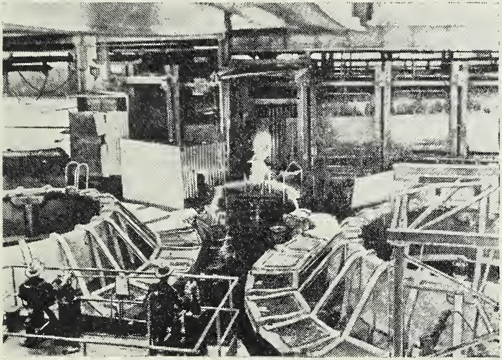
$$[2CuFeS_2 + 13O = 2CuO + Fe_2O_3 + 4SO_2]$$
$$4CuFeS_2 + 13O_2 = 4CuO + 2Fe_2O_3 + 8SO_2$$

The ferric oxide thus produced is used in the smelting of iron. The copper oxide, however, is far more valuable. To extract the metal, the oxide is roasted with about one-eighth its weight of common salt. This causes the production of cupric chloride. The latter is then dissolved out with water, and scrap iron is added to precipitate the copper ($CuCl_2 + Fe = FeCl_2 + Cu$).

Refinement by Electrolysis. At the present time very large quantities of copper are used for making electric cables, because *pure* copper is an excellent conductor of electricity. Its conductivity is greatly reduced, however, by the presence of very small amounts of impurity. Hence there is a great demand for copper of a high degree of purity.

Accordingly, the copper obtained by the various processes already mentioned is refined electrolytically. Some account of the process has already been given on p. 402, but a few details may be added here.

The tanks are made of wood or concrete, usually lined with lead, and the electrolyte with which they are filled consists of a solution of copper sulphate acidified with sulphuric acid. This solution is heated and slowly circulated through the tanks. The anodes consist of slabs each weighing several hundredweights, cast from the smelted product. The illustration below shows how the latter is run into trays serving as moulds. These are carried on a sort of wheel, which turns at a slow adjusted rate so that each tray is filled with the molten metal before it passes on. The cathodes consist of thin 'starting sheets' of pure copper. On the next page you can see them being lowered into the electrolytic tank.

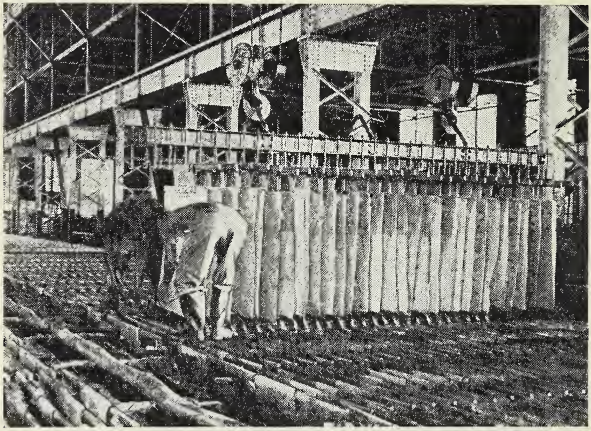


By courtesy of Copper Development Association

Anode casting wheel

The cathodes, originally weighing only 10 lb. or so, slowly increase in weight until after about a fortnight they will weigh from 2 to 2½ cwt. They are then withdrawn and replaced with fresh starting sheets. The copper so deposited is of a high degree of purity, about 99·95 per cent.

A large tank-house would contain perhaps 1500 tanks, each fitted with about thirty-six anodes and thirty-seven cathodes (anodes and cathodes alternating). Thus in all there may be more than 100,000 anodes and cathodes, making a very impressive assembly. We may add that about 85 per cent. of the world's output of copper is now electrolytically refined.



By courtesy of Anglo-American Corporation of South Africa Ltd.

Lowering starting sheets into electrolytic tank

Properties and Uses. Copper is very malleable and ductile, it possesses great tensile strength, and it is not readily corroded. These properties cause it to be used, in the form of sheet and wire, for a great variety of purposes. The condenser tubes of locomotives are often made of copper, partly because (as we saw on p. 97) it is not acted upon by steam at any temperature, and partly because, with the exception of silver, it is the best conductor of heat of all the metals. The latter property makes it a suitable material for kettles, evaporating pans, etc. The use of copper for making electric cables has already been mentioned.

Copper is often used as a sheathing for the hulls of wooden ships. This prevents timber worms from boring into the wood, and it also reduces the rate at which the usual overgrowth of barnacles, sea-weed, etc., is formed (an overgrowth which has to be removed from time to time because of its effect on the speed of the ship). No doubt the copper, reacting with the various salts present in sea-water, is constantly forming small quantities of copper sulphate, copper chloride, etc., and it is probably the poisonous nature of these substances which helps to keep sea organisms at bay.

Copper forms some extremely useful alloys, including brass, Dutch metal and bronze. Brass and Dutch metal have been mentioned in previous chapters (pp. 456, 251) and bronze at the beginning of the present one.

In the absence of air, copper is not acted upon in the cold by either sulphuric or hydrochloric acid, whether dilute or concentrated. This result is, of course, just what we should expect if we keep in mind that it comes below hydrogen in the electrochemical series (p. 391). The fact that copper has no action on steam even when strongly heated is also related to its low position in the series.

The action of *hot* concentrated sulphuric acid is dealt with elsewhere (p. 297), and so is that of nitric acid, dilute and concentrated (pp. 346, 349).

Copper Sulphate, $CuSO_4 \cdot 5H_2O$, is often known as *blue vitriol* or *blue-stone*. On the large scale it is manufactured by the action of dilute sulphuric acid on copper in the presence of air:—

$$[Cu + H_2SO_4 + O = CuSO_4 + H_2O]$$
$$2Cu + 2H_2SO_4 + O_2 = 2CuSO_4 + 2H_2O$$

It is easily prepared in the laboratory by warming copper oxide with dilute sulphuric acid:—

$$CuO + H_2SO_4 = CuSO_4 + H_2O$$

In your own practical work you very likely made it when you were preparing sulphur dioxide by heating copper with concentrated sulphuric acid (p. 278).

When heated to 100° C. copper sulphate loses four of its five molecules of water of crystallisation. To drive off the remaining molecule the temperature must be kept for some time at about 250° C. (see p. 105). You have no doubt often used the white, anhydrous substance in testing for water, which re-hydrates it and so restores the blue colour.

When *strongly* heated, copper sulphate is decomposed into copper oxide and sulphur trioxide ($CuSO_4 = CuO + SO_3$). That is one reason why you must not use a full flame when heating a weighed quantity of blue vitriol in a crucible to find the percentage of water of crystallisation.

If after finishing the experiment just mentioned you empty the crucible, you will probably find that the substance next to the bottom of the crucible (and which has been rather overheated) is *yellow*. This yellow substance has been found to have the composition expressed by the formula $CuSO_4 \cdot CuO$, and is said to be a *basic sulphate*.

This is an example of a ***basic salt***, which we may conveniently regard as *a compound of a normal salt with the base* (*oxide or hydroxide*) *from which that salt is derived*. We shall presently come across an important basic salt known as 'white lead.' This is basic lead carbonate, and has the formula $2PbCO_3 \cdot Pb(OH)_2$.

It would be well at this point to read again what was said about *acid salts* on p. 299. Writing acid sodium sulphate ($NaHSO_4$) as $Na_2SO_4 \cdot H_2SO_4$, we see that it may be regarded as a compound of the normal salt with the *acid* from which that salt is derived.

To return to copper sulphate, we have already seen that it is used in connection with the deposition of copper in the process of electrolysis. Mixed with lime (forming 'Bordeaux mixture') it is also used for spraying vines, potatoes, etc., to prevent fungus growths. It has a number of other uses.

Cupric Oxide, CuO, is *not* easily made, in quantity, by heating copper in air (otherwise the working life of a copper kettle would be a very short one). In such circumstances the copper oxidises on the surface only, and the layer of oxide protects the metal underneath.

It is readily prepared by first dissolving copper in nitric acid to make the nitrate (we have already had the equations in connection with nitric oxide and nitrogen dioxide, pp. 346, 349) and then heating the nitrate until brown fumes cease to be evolved.

$$[Cu(NO_3)_2 = CuO + 2NO_2 + O] \qquad 2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$$

Still another method is to add sodium hydroxide to a solution of a copper salt such as the sulphate. This gives a pale blue precipitate of copper hydroxide:—

$$CuSO_4 + 2NaOH = Na_2SO_4 + Cu(OH)_2$$

When boiled this precipitate becomes black and granular, being converted into a slightly hydrated oxide ($4CuO \cdot H_2O$). This is easily filtered, and when heated to redness is converted into the oxide CuO.

You have no doubt *reduced* copper oxide to copper by means of hydrogen or coal-gas. As we learnt in Chapter 18, the latter is a mixture composed chiefly of hydrogen, methane and carbon monoxide, and the chemical changes would be represented by the equations

$$CuO + H_2 = Cu + H_2O$$
$$4CuO + CH_4 = 4Cu + CO_2 + 2H_2O$$
$$CuO + CO = Cu + CO_2$$

It is clear that in every case the copper oxide is acting as an oxidising agent.

The reactions mentioned in the latter half of this section ($CuSO_4 \rightarrow Cu(OH)_2 \rightarrow CuO \rightarrow Cu$) evidently give us a means of obtaining copper from copper sulphate without using electrolysis.

Copper Carbonate. The *normal* carbonate of copper ($CuCO_3$) is not known, but a number of basic carbonates are met with. The bright green mineral *malachite*, for instance, is a basic carbonate having the formula $CuCO_3 \cdot Cu(OH)_2$.[1] Still another basic carbonate is produced as a light blue precipitate when a solution of sodium carbonate is added to one of copper sulphate.

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[1] The green *patina*, formed on copper which has been exposed to the air, was for a long time believed to be a basic carbonate, but has now been shown to be mainly a basic sulphate, $CuSO_4 \cdot 3Cu(OH)_2$.

When any of these basic carbonates are heated, copper oxide is left behind, e.g.

$$CuCO_3{\cdot}Cu(OH)_2=2CuO+CO_2+H_2O$$

Cupric and Cuprous Compounds. So far we have spoken simply of 'copper sulphate,' 'copper oxide,' etc., but these terms are really a little ambiguous. Copper forms *two* series of compounds—*cupric* compounds in which the metal has a valency of two, and *cuprous* compounds in which its valency is one, e.g. cupr*ic* oxide has the formula CuO, while cupr*ous* oxide would be represented by Cu_2O. We had a somewhat similar double series in the case of the iron compounds, but there the valencies were three and two instead of two and one respectively.

Strictly speaking, then, 'copper sulphate' ($CuSO_4$) is *cupric* sulphate, and 'copper oxide' (CuO) is *cupric* oxide. The '-*ic*' compounds are met with so much oftener than the '-*ous*' that, if no special termination is used, it is understood that the '-*ic*' compound is meant.

You may have met with cuprous oxide (Cu_2O) when doing experiments on the Law of Multiple Proportions. It is a red powder, and is sometimes added to molten glass to make 'ruby glass.'

We have met with cupr*ic* sulphide as the black precipitate formed when hydrogen sulphide is passed through a solution of copper sulphate. When strongly heated out of contact with air, half of its sulphur is driven off, and cupr*ous* sulphide remains:—

$$2CuS=Cu_2S+S$$

Keeping this reaction in mind, we may be sure that if a sulphide of copper is being produced at high temperatures, it is the -*ous* compound that will be formed. Thus if a spiral of copper wire is made red-hot and plunged into the vapour of boiling sulphur, cuprous sulphide is produced as a black, brittle substance.

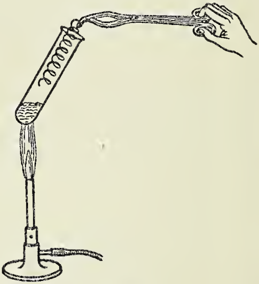


FIG. 38/1

Formation of cuprous sulphide

Copper Compounds from Copper. To make copper compounds from copper, the simplest method in most cases is to begin by making the *oxide* (via the nitrate, as already described). From this we can easily make a solution of the *sulphate* by warming with dilute sulphuric acid, and we use this solution to obtain *insoluble compounds* by precipitation (e.g. the sulphide by using hydrogen sulphide, the hydroxide by using sodium hydroxide solution and so on).

To obtain the **chloride** (soluble), we should dissolve the oxide in hydrochloric acid, concentrate the solution and allow to crystallise.

Tests for Copper Compounds. Copper compounds give a green colour to the bunsen flame, but if the chloride is present (as it will be if we carry out the flame test in the usual way, first moistening with hydrochloric acid) the colour is blue.

Everybody has noticed the blue colour produced when a little common salt is sprinkled on a clear red fire. The explanation is probably that coal always contains traces of copper compounds (especially the sulphide), and these are converted by the salt into cuprous chloride, Cu_2Cl_2,[1] which vaporises and gives the characteristic colour to the flame.

Another test is to put a little clean iron wire into a solution of the compound. After a few seconds a pinkish deposit of copper will be observed on the wire.

The reaction of a soluble copper salt with sodium hydroxide solution (pale blue precipitate turning black on boiling) is also characteristic.

LEAD

Occurrence and Extraction. Lead is found chiefly as *galena*, PbS. The ore is usually mixed up with much earth, rock, etc., and has to be concentrated before smelting. This is usually done by the 'froth flotation process' (p. 462). The ore thus concentrated is now *sintered*, a roasting operation in which it is largely converted into semi-fused lumps of lead oxide, with the production of sulphur dioxide, which is led off as a by-product:—

---

[1] At high temperatures cupric chloride, $CuCl_2$, would be decomposed. Cf. cupric and cuprous sulphide in the previous paragraph.

$$[PbS + 3O = PbO + SO_2] \qquad 2PbS + 3O_2 = 2PbO + 2SO_2$$

The sintered material is now heated in a blast furnace with coke and limestone, the latter helping to form a fluid slag (cf. extraction of iron, p. 443). A little scrap iron is often added. The lead oxide is reduced, partly by carbon monoxide formed from the coke, partly by the coke itself:—

$$PbO + CO = Pb + CO_2$$
$$2PbO + C = 2Pb + CO_2$$

The sintered material always contains some unchanged sulphide, and this is reduced by the scrap iron already mentioned ($PbS + Fe = FeS + Pb$).

At this stage the lead contains various impurities, but we will not go into the question of how they are removed. It is interesting to notice that lead always contains some silver, and if this is present only to the extent of 2 oz. in every ton, it pays to extract it. The final product is usually at least 99·99 per cent. pure lead.

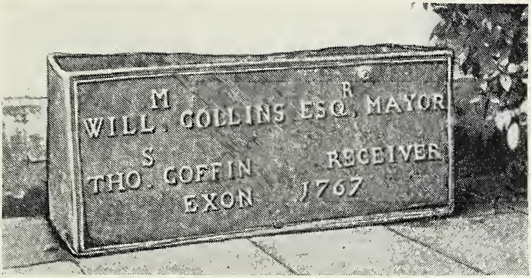
Properties. Freshly-cut lead has a silvery, slightly bluish surface, but it soon becomes dull owing to the production of a film of carbonate (the oxide first formed reacting with atmospheric carbon dioxide). This carbonate protects the lead beneath from further change, with the result that articles made of lead are wonderfully little affected (except on the surface) by exposure to the atmosphere. Thus the photograph shows a cistern which was made nearly 200 years ago, and is little the worse for wear. Much more striking is the fact that many of the lead pipes which the Romans used at Bath nearly 2000 years ago are still in remarkably good condition.

It is much used by builders, e.g. to provide the 'flashing' that gives a watertight joint between chimney and roof. It is also employed very largely as the sheathing for electric cables, and in making the plates of accumulators. Alloyed with tin in various proportions it gives one or other of the solders (e.g. *soft-solder* consists of the two metals in equal parts), while with antimony and tin it forms *type-metal*. But anything like a full list of the uses of lead would be very long indeed.

Pure water with oxygen in solution has a perceptible effect on lead. The dissolved gas first oxidises the metal, and the lead oxide is then converted by the water into lead hydroxide, which is slightly soluble:—

$$PbO + H_2O = Pb(OH)_2$$

Now soluble lead compounds are poisonous, so it looks as though it would be dangerous to drink water which has passed through lead pipes. In practice the difficulty very seldom arises.[1] Ordinary drinking-water is never perfectly 'soft'—it contains at least a little calcium sulphate and bicarbonate in solution (p. 180). The result is that the lead pipes become coated with a thin film of lead sulphate and lead carbonate, and this film forms a perfect barrier between the water on one side and the lead on the other.[2]



Eighteenth-century lead tank in the Rougemont Gardens, Exeter

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[1] The case of Glasgow, which uses the very pure water of Loch Katrine, is sometimes quoted to the contrary. It is said that the water has to be artificially hardened in order that it may not attack the lead pipes. Enquiry shows that there is no truth in the statement. The water is not treated in any way—it is not even filtered.

The case of water which has been lying for a long time in a lead-lined tank is different. It would probably be unfit for drinking. Further, it has been shown that the presence of certain salts—notably ammonium nitrate—greatly increases the rate at which water attacks lead.

[2] An experiment relating to the action of water on lead is described on pp. 220–1 of the author's *School Course of Practical Chemistry* (Bell).

Lead is very resistant to the action of hydrochloric and sulphuric acids, and this may be due in part to the fact that it is only *just* above hydrogen in the electrochemical series, but the chief cause is no doubt the insolubility of lead chloride and lead sulphate. You will remember that the chambers used in the manufacture of sulphuric acid are made of this metal. Lead dissolves easily when warmed with nitric acid, lead nitrate being produced and oxides of nitrogen (nitric oxide predominating if the acid is dilute, nitrogen dioxide if it is concentrated; cf. the similar reactions with copper, pp. 346, 349).

Oxides of Lead. Five oxides of lead are known, and of these we must consider three.

Lead monoxide ('litharge'), PbO, is the yellow or reddish-yellow substance formed when lead is heated in air. Traces of it can be seen in the plumber's melting-pot when street pipes are being repaired. It has many uses, one of which is in the glazing of pottery (p. 384). It is also used in making flint-glass.

Lead oxide is often added to paint to speed up the process of 'drying.' The drying really consists in the combination of the linseed oil with atmospheric oxygen, a solid compound called 'linoxyn' being formed. The lead oxide acts as a catalyst.

The monoxide is the most stable oxide of lead, and is formed when any of the other oxides are strongly heated.

Red lead, Pb_3O_4,[1] is made by heating the monoxide in air at a temperature of about 400° C.

$$[3PbO + O = Pb_3O_4] \qquad 6PbO + O_2 = 2Pb_3O_4$$

At a somewhat higher temperature (470°) the action is reversed.

When warmed with dilute nitric acid, red lead at once turns brown owing to the formation of lead dioxide. On filtering, the dioxide remains behind, while lead nitrate passes through and can easily be crystallised out.

---

[1] The percentage of oxygen in ordinary specimens of red lead differs considerably from that required by the formula Pb_3O_4.

To arrive at the equation, it is best to regard Pb_3O_4 as $2PbO + PbO_2$. We may then suppose that the monoxide PbO reacts in the ordinary way to form the nitrate, while the dioxide PbO_2 is unchanged, i.e.

$$\begin{array}{llll} & PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O & & \text{(i)} \\ \text{or} & 2PbO + 4HNO_3 = 2Pb(NO_3)_2 + 2H_2O & & \text{(ii)} \\ & PbO_2 = PbO_2 & & \text{(iii)} \end{array}$$

Adding (ii) and (iii),

$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 + 2H_2O$$

Like the monoxide, red lead is used in making flint glass. It is also much used as a red paint.

Lead dioxide or *peroxide*, PbO_2, may be prepared as indicated above. It reacts vigorously with sulphur dioxide, forming lead sulphate

$$PbO_2 + SO_2 = PbSO_4$$

It is chiefly used as a filling in the lead plates of accumulators.

Action of Heat, Hydrogen and of Hydrochloric Acid on the Oxides of Lead. Lead monoxide is very stable. It melts when strongly heated, but undergoes no chemical change.

The other oxides easily decompose, oxygen being evolved while the monoxide is left behind. You should be able to make up the equations for yourself.

All the oxides of lead, when heated in a current of hydrogen, are readily reduced to the metal.

When heated with hydrochloric acid, lead chloride and water are formed in all cases, and except in the case of the monoxide, chlorine is evolved

$$\begin{aligned} PbO + 2HCl &= PbCl_2 + H_2O \\ Pb_3O_4 + 8HCl &= 3PbCl_2 + 4H_2O + Cl_2 \\ PbO_2 + 4HCl &= PbCl_2 + 2H_2O + Cl_2 \end{aligned}$$

(*N.B.* In writing the equations, arrange that the amount of hydrogen shall be just enough to turn all the oxygen into water, e.g. with Pb_3O_4 take 8HCl. Cf. p. 250.)

Lead Chloride, $PbCl_2$. We have just seen that this may be made by heating any of the oxides with hydrochloric acid.

To obtain the substance in a pure state the residue is washed once or twice by decantation to remove surplus hydrochloric acid, and is then boiled with water. The unchanged lead oxide remains behind and is allowed to settle, after which the hot solution is poured off into another test-tube. On cooling under the tap lead chloride readily crystallises out—'like a miniature snowstorm.'

As lead chloride is only slightly soluble in water, we can also readily prepare it by the method of double decomposition (p. 153). We add a solution of a chloride to a solution of a lead salt, e.g. the nitrate or acetate:—

$$Pb(NO_3)_2 + 2NaCl = 2NaNO_3 + PbCl_2$$

Lead Iodide is prepared similarly, a solution of potassium iodide being usually employed:—

$$Pb(NO_2)_2 + 2KI = 2KNO_3 + PbI_2$$

Lead Sulphate. This has already been discussed under 'Some Important Sulphates,' p. 300. We may add that as it is a highly insoluble salt it is readily prepared by the method of double decomposition. We add dilute sulphuric acid (i.e. hydrogen sulphate) or a solution of some other sulphate (e.g. magnesium sulphate) to a solution of a lead salt such as the nitrate:—

$$Pb(NO_3)_2 + MgSO_4 = Mg(NO_3)_2 + PbSO_4$$

Lead Carbonate. The normal carbonate, $PbCO_3$, may be prepared by adding a solution of sodium *bi*carbonate to one of lead nitrate or other soluble lead salt. A much more important compound, however, is the *basic* carbonate, $(PbCO_3)_2 \cdot Pb(OH)_2$, commonly known as *white lead.* This mixes well with linseed oil, and the white paint thus formed possesses great 'body' or covering power. It has already been explained, however, that on exposure to air containing traces of hydrogen sulphide it gradually darkens, owing to the fact that lead sulphide is black. In this way many of the 'old masters' had ceased to be recognisable. They have been restored by the cautious application of hydrogen peroxide (H_2O_2), which oxidises the black sulphide to white lead sulphate:—

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O$$

Basic Salts and the Electrochemical Series. The basic carbonate, *white lead*, has just been mentioned, and a few pages back (p. 467) a basic copper carbonate, $CuCO_3 \cdot Cu(OH)_2$, was noted.

It is worth observing that the metals near the top of the electrochemical series (p. 391)—potassium, sodium, calcium, etc.—tend to form (besides their normal carbonates) *acid* carbonates, usually called bicarbonates, such as $NaHCO_3$ and $Ca(HCO_3)_2$. We may regard them as compounds of the normal carbonates with the parent acid. $NaHCO_3$, for instance, may be regarded as $Na_2CO_3 \cdot H_2CO_3$.

At the lower end of the series acid carbonates are hardly ever formed. The tendency is to form *basic* carbonates such as those mentioned above. In fact, some of these feebly electropositive metals, e.g. copper, do not form a normal carbonate.

In view of the tendency we are discussing—i.e. from acid-carbonate to basic-carbonate formation—it is reasonable to expect that as we descend the list, acid carbonates would become less stable, and on the whole this is true. Thus the acid carbonates of sodium and potassium are fairly stable solids, those of calcium and magnesium exist only in solution, and acid carbonates of copper and lead do not exist at all.

To a less extent we notice what we may call the 'acid-to-basic' tendency in the case of some other salts such as the sulphates. Thus sodium and potassium form well-marked acid sulphates ('bisulphates') such as $NaHSO_4$ ($=Na_2SO_4 \cdot H_2SO_4$) but no basic sulphates, while copper forms basic sulphates (e.g. $CuSO_4 \cdot CuO$, p. 466) but no acid sulphate.

Tests for Lead. The formation of some of the compounds just mentioned—chloride, iodide, etc.—may be used as tests for lead, or strictly speaking for lead ion, Pb^{++}. As a useful test, we must dismiss the formation of the carbonate, because so many metals besides lead form insoluble carbonates. There are also one or two other metals (e.g. barium, p. 300) which form white insoluble sulphates, and several which form black insoluble sulphides (e.g. copper).

However, *taken together*, the sulphate and sulphide tests are quite good, for lead is the only common metal which forms a black insoluble sulphide *and* a white insoluble sulphate.

The chloride test, carried out carefully, is sufficient in itself, for the crystallising out from boiling water is very characteristic. The same may be said of the iodide test.

It is sometimes necessary to find whether any lead compound (derived from the pipe or tank) is present in a sample of drinking-water. We must expect that the amount present, if any, will be very small indeed, so we begin by *concentrating* our sample. Suppose we evaporate 5 litres of the water until only 5 c.c. remain. Any lead compound originally present is still there, but the concentration is increased a thousandfold. We now pass hydrogen sulphide through half of the residue, and add one drop of pure sulphuric acid to the other. If lead is present, a dark precipitate of lead sulphide will be produced in the one case and a white one of lead sulphate in the other—and if that happens the local waterworks surveyor should be informed at once!

The tests mentioned above all involve the use of solutions. Here is a 'dry test.'

If a solid lead compound is mixed with sodium carbonate and heated on a charcoal block with a blowpipe flame, a bead of lead is obtained. This can be distinguished from other beads (e.g. silver) by the fact that it is soft enough to mark on paper. On the charcoal round the bead there will be a yellow deposit of lead monoxide, PbO.

The sodium carbonate acts partly as a *flux*, i.e. it melts, and the lead compound, being distributed throughout the molten carbonate, undergoes chemical change more readily than if it were concentrated in one place. Further, the lead compound by double decomposition with sodium carbonate forms lead carbonate, which under the action of heat yields the oxide ($PbCO_3 = PbO + CO_2$).

Preparation of Lead Compounds. It will provide a useful review of much of what we have learnt in the past five or six pages if we suppose ourselves to start from lead and try to make some of the compounds mentioned.

We might well begin by heating the metal with dilute nitric acid to make the nitrate. From separate portions of the solution we could quickly prepare the chloride, iodide, sulphate, sulphide and carbonate, by double decomposition with hydrochloric acid, potassium iodide, etc.

We could crystallise out some of the nitrate and heat it to obtain lead monoxide. Prolonged heating in air at about 400° C. would give us red lead, and by warming the latter with dilute nitric acid we could obtain the dioxide.

MERCURY

Occurrence and Extraction. Mercury occurs in Nature as the sulphide HgS, known as *cinnabar*, a red or black mineral found in various parts of the world, but chiefly in Spain and Italy. In Texas the Indians formerly used the (red) material for painting their faces.

Earthy material would be considered very rich in cinnabar if it contained as much as 8 per cent. Usually the proportion is much less, and a good deal of hand-picking has to be resorted to in order to obtain an ore of reasonable concentration. This is one reason for the high price of mercury.

The methods used in obtaining the metal differ considerably in detail, but practically all depend on the fact that when the sulphide is heated with a good supply of air, the sulphur is converted into sulphur dioxide and the mercury is set free

$$HgS + O_2 = SO_2 + Hg$$

The mercury is converted into vapour, which passes, along with the sulphur dioxide, into suitable condensing chambers. Here the mercury liquefies, while the sulphur dioxide, of course, passes on.

This mercury is purified (roughly) by forcing it through a bag of chamois leather. For most scientific purposes however, a much purer product is required, and this is obtained by distilling the mercury under reduced pressure.

Mercury very readily dissolves small quantities of copper, lead and other metals, and so it often becomes impure after being in ordinary laboratory use for some time. A fairly effective method of purifying such mercury is to shake it up with a solution of mercurous nitrate. The copper, lead, etc., being higher than mercury in the electrochemical series (p. 391), displace mercury from this solution. The unwanted metals are now in solution as nitrates, and can easily be washed away.

A useful test for the purity of mercury is to see whether it leaves any 'tail' when allowed to roll over a surface of clean glass or porcelain.

Properties and Uses. On account of its high density (13·6) mercury is used in the manufacture of barometers. Its high boiling-point (357° C.) and low freezing-point ($-39°$ C.), together with its regularity of expansion on heating, make it a very suitable liquid for use in thermometers.

Mercury is chiefly useful, however, on account of its power of forming alloys, or ***amalgams*** as they are called, with other metals. Thus one process for the extraction of gold is to allow this metal to come into contact with mercury. A gold amalgam is obtained, and when this is distilled, the mercury passes over and can be used again, while the gold remains behind.

The zinc plates used in a voltaic cell are brushed over with mercury. This forms a coating of zinc amalgam on the surface, and prevents the zinc from being dissolved except when the circuit is actually closed.

Tin amalgam was formerly used in the backing of mirrors, but the modern process is to obtain a deposit of real silver by reduction of a solution of silver nitrate placed in contact with the glass.

Sodium amalgam is sometimes used in the laboratory as a reducing agent. In presence of water, hydrogen is liberated exactly as in the case of sodium itself, but the action is much more gentle. Mercury remains behind, and can be used of course for making further quantities of amalgam.

Mercury, however, does not readily amalgamate with iron, and so the mercury of commerce is marketed in screw-stoppered iron bottles, each containing 76 lb.

Important Compounds

Mercuric Oxide, HgO, has already been mentioned (p. 76). It is of great importance in connection with the early history of oxygen.

Mercuric Chloride, $HgCl_2$ ('corrosive sublimate'), like other compounds of mercury, is very poisonous, but is used in minute quantities in medicine. The surgeon uses a very dilute solution of it (1 part in 1000 parts of water) for sterilising his hands and his instruments—it kills bacteria.

Several other compounds of mercury are used in medicine. They were introduced by Paracelsus (*c.* 1490–1541), a famous physician who taught that the great object of chemistry was not to turn base metals into gold (a view almost universally held before his time), but to prepare medicines. No doubt he did his best, but most of us would have hesitated to take pills and medicine from a doctor who was making the very first experiments with compounds of mercury.

Questions

1. 'An easy calculation shows that pure copper pyrites would contain nearly 35 per cent. of copper' (p. 462). Work out this percentage accurately, to one decimal place. (Cu=63·6; Fe=55·8; S=32·1.)

2. Describe *two* laboratory methods (excluding electrolysis), with an outline of experimental details, which you could use to prepare a sample of copper from copper sulphate as the starting material.

Give a brief account of the refining of copper by electrolysis.

State *two* uses of copper and say what properties of the metal account for these uses. *Dur.*

3. Given some metallic copper, how would you prepare: (*a*) copper nitrate crystals from the metal; (*b*) copper oxide from the nitrate; (*c*) copper sulphate crystals from the oxide?

Give equations for the reactions you describe.

If you used 10 gm. of copper in (*a*) and the whole of this was eventually turned into copper sulphate crystals ($CuSO_4 \cdot 5H_2O$), what weight of crystals, to the nearest gram, would you obtain?

2·88 gm. of red oxide of copper (cuprous oxide) when reduced leaves 2·56 gm. of copper. Calculate: (*d*) the equivalent weight; (*e*) the valency of copper in cuprous oxide. ($H=1$; $O=16$; $S=32$; $Cu=64$.) *Lond.*

4. A blue crystalline substance was gently heated in a hard-glass tube. Moisture was seen to condense on the side of the tube, and the substance lost its crystalline shape and blue colour. When heated more strongly, the substance darkened in colour, and dense white fumes were evolved.

A solution of the original substance was made in distilled water, and successive portions reacted as follows: (*a*) caustic soda solution produced a light blue gelatinous precipitate that turned black when the mixture was heated; (*b*) sodium carbonate solution produced a greenish-blue precipitate; (*c*) ammonia solution (0·88) first produced a light blue precipitate that dissolved in an excess of the reagent giving a deep blue coloured solution; (*d*) barium chloride solution produced a white precipitate that proved to be insoluble in an excess of hydrochloric acid.

Give the chemical name and formula of the original blue crystalline substance, and account for all the changes described, giving equations where possible. *Lond.*

5. Describe two tests for the presence of copper ion, giving equations where possible.

6. In what form is lead most commonly found in Nature? Describe and explain how the metal is extracted on a commercial scale.

Mention some of the chief uses of metallic lead, pointing out how these uses are related to its properties.

7. A scarlet powder *A* when warmed with dilute nitric acid produces a brown substance *B* that is removed by filtration. The filtrate on treatment with potassium chromate (K_2CrO_4) solution gives a yellow precipitate *C*. On heating *B* in a tube, a gas is evolved that ignites a glowing splinter of wood, and a yellow solid *D* remains in the tube.

When *D* is strongly heated in a stream of hydrogen, drops of a colourless liquid condense at the cooler end of the tube through which hydrogen passes, and globules of a metal *E* are produced. These globules solidify on cooling and are found to be malleable and to mark paper.

When *either* *A* or *B* is heated with hydrochloric acid a greenish gas that turns starch iodide paper blue is evolved. The resulting solution deposits white crystals, *F*, on cooling.

Name the substances *A* to *F*. Give equations and account for the various changes that are described. *Lond.*

8. 1·50 gm. lead was dissolved in nitric acid and precipitated as sulphate by the addition of dilute sulphuric acid. 2·20 gm. of lead sulphate was formed. Calculate the equivalent of lead, given that the molecular weight of sulphuric acid is 98. (H=1.)
Dur. (*part*)

9. Prepare a four-column table as indicated below and fill it in. Where a chemical reaction occurs, give the equation.

Oxides of lead

Oxide and Formula	*Action of*		
	Heat	*Hydrogen*	*Hydrochloric acid*

10. What is *cinnabar*? How is mercury obtained from it?

11. Show that the properties of mercury are consistent with its low position in the electrochemical series (p. 391).

12. What do you mean by *double decomposition*? Give three examples.

13. With the help of the Index, make a list of the *catalysts* mentioned in this book, and of the reactions in which they are employed, arranging your answer in two parallel columns.

CHAPTER 39

VOLUMETRIC ANALYSIS

In ***qualitative*** analysis we have to find the constituents of a given substance or mixture, but we are not concerned with the *quantities* of those constituents. In ***quantitative*** analysis we have to determine those quantities. Various methods are in use, and one of them is the ***volumetric*** method. It consists in arranging for a reaction to take place between two solutions under such conditions that there is no excess of either one or the other. The strength of one of the solutions being known, that of the other can then be calculated. This is a very general statement, but the meaning will become clearer as the chapter proceeds.

In volumetric analysis the strength of a given solution always has a close relation to the *equivalent* of the substance concerned, so before proceeding further we must be clear about the meaning of this term. In Chapter 6 we dealt with the equivalent of *elements*. We now need to consider the equivalent of *compounds*—to begin with, of acids and bases.

All acids contain hydrogen that can be replaced by a metal, e.g. the hydrogen in sulphuric acid, H_2SO_4, can be replaced by zinc, giving us zinc sulphate, $ZnSO_4$. Adding up the molecular weight of sulphuric acid we get $H_2=2$, $S=32$, $O_4=64$, total 98. 98 gm. of sulphuric acid contain *two* grams of replaceable hydrogen, therefore 49 gm. would contain *one* gram, and 49 is said to be the *equivalent* of sulphuric acid. *The* ***equivalent of an acid*** *is the number of grams of that acid which contains one gram of hydrogen replaceable by a metal.*

(The last four words are inserted because some acids contain hydrogen which is *not* replaceable by a metal, as well as hydrogen which *is*. Acetic acid, for instance, $C_2H_4O_2$, contains four atoms of hydrogen, but only one of these is replaceable by a metal. It is only this one that 'counts' for our present purpose. Compare p. 298.)

An acid is neutralised by a base. ***The equivalent of a base** is the number of grams of the base required to neutralise the equivalent of an acid.* E.g. consider the base sodium hydroxide, NaOH. It neutralises sulphuric acid according to the equation

$$\begin{array}{l} H_2\quad S\quad O_4 + 2Na\quad O\quad H = Na_2SO_4 + 2H_2O \\ \underbrace{2+32+64}_{98}\quad \underbrace{2(23+16+1)}_{80} \end{array}$$

The numbers given show that to neutralise 98 gm. of sulphuric acid we require 80 gm. of sodium hydroxide. Therefore to neutralise 49 gm. (the equivalent weight) we require 40 gm. 40 is therefore the equivalent of sodium hydroxide.

We obtain the same result if we consider the equation according to which sodium hydroxide neutralises *hydrochloric* acid.

$$\begin{array}{l} H\quad Cl + Na\quad O\quad H = NaCl + H_2O \\ \underbrace{1+35{\cdot}5}_{36{\cdot}5}\quad \underbrace{23+16+1}_{40} \end{array}$$

Here 36·5 is the equivalent of hydrochloric acid (because 36·5 gm. contains 1 gm. of replaceable hydrogen). To neutralise this amount we require 40 gm. of sodium hydroxide, the equivalent of which is therefore 40, as before.

In volumetric analysis a solution of sodium (or potassium) carbonate is often used to neutralise an acid. A carbonate is not a base, but its equivalent is defined in the same way. Consider sodium carbonate reacting with hydrochloric acid

$$\begin{array}{l} 2H\quad Cl + Na_2\quad C\quad O_3 = 2NaCl + H_2O + CO_2 \\ \underbrace{2(1+35{\cdot}5)}_{73}\quad \underbrace{46+12+48}_{106} \end{array}$$

To react with 73 gm. of acid we require 106 gm. of sodium carbonate, and therefore to react with 36·5 gm. (the equivalent of hydrochloric acid) we require 53 gm. of sodium carbonate. 53 then is the required equivalent.

Notes. (1) The equivalent is a *number*, not a weight. The corresponding weight in grams is called the ***gram-equivalent.*** Thus the equivalent (or equivalent weight) of sodium carbonate is 53, but its gram-equivalent is 53 gm.

(2) A useful working rule for finding the equivalent of a base or carbonate is as follows. Imagine the metal to be replaced by sufficient hydrogen to turn the base into water (or the carbonate into carbonic acid). Then divide this number of hydrogen atoms into the molecular weight, e.g. *base*, calcium hydroxide, $Ca(OH)_2$. To turn the base into water we should have to replace the metal with *two* hydrogen atoms. Therefore the equivalent is the molecular weight (74) divided by 2.

Sodium carbonate, Na_2CO_3. To turn this into carbonic acid we should have to replace the sodium by *two* hydrogen atoms. Hence we divide the molecular weight by 2. In the case of sodium bicarbonate, $NaHCO_3$, only *one* hydrogen atom is needed to replace the sodium, so the equivalent is the same as the molecular weight.

Normal Solutions. *A **normal solution** is one which contains a gram-equivalent of the solute per litre.* Thus we could make a normal solution of sodium carbonate by weighing out 53 gm. of the anhydrous carbonate (53 being the equivalent), dissolving in water and making up to 1 litre. (Notice that this is not quite the same thing as dissolving 53 gm. of the carbonate in 1 litre of water.)

The terms *semi-normal*, *deci-normal*, etc., almost explain themselves. A semi-normal solution, for instance, is half as strong as a normal solution.

Suppose we had a normal solution of sodium hydroxide, 40 gm. per litre, and one of hydrochloric acid, 36·5 gm. per litre.

Now 40 gm. of sodium hydroxide will neutralise 36·5 gm. of hydrochloric acid (if you read the definition of 'equivalent of a base' again, you will see that that is how the number 40 was obtained). Therefore 1 litre of normal sodium hydroxide, containing 40 gm., will neutralise 1 litre of normal hydrochloric acid, containing 36·5 gm. Similarly *any* volume of normal sodium hydroxide solution will neutralise an *equal* volume of normal hydrochloric acid solution, and so for any other acids, bases and carbonates. The principle is an extremely important one, and so had better receive formal statement. *Normal solutions are equivalent to one another, volume for volume.*

Preparation of Standard Solutions. Any solution of known strength is a 'standard solution.' The chief difficulty in preparing standard solutions of acids and alkalis is that the substance concerned often contains a rather uncertain quantity of water. 'Pure' sulphuric acid, for instance, usually contains from 2 to 5 per cent. Further, the amount of moisture present may increase even while we are handling it, a notable case being that of sodium hydroxide. A common method is to begin by preparing pure anhydrous sodium carbonate, by heating pure sodium bicarbonate until it ceases to change in weight[1] ($2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$). As already explained, the equivalent of sodium carbonate is half the molecular weight and comes to 53. We therefore weigh out 53 gm. of the prepared carbonate, dissolve in water, and make up to 1 litre. In practice $\frac{1}{4}$ litre (from 13·25 gm.) is usually sufficient.

We now prepare a solution of an *acid* (say sulphuric) of rather more than normal strength, say 60 gm. per litre (normal being 49). This more than allows for the water present. At this stage the weighing, etc., may be quite rough.

We next make a careful titration[2] of the acid solution against that of sodium carbonate. If the acid had been normal, the volume required would have been equal to that of the carbonate ('normal solutions equivalent to one another, volume for volume'). The acid is stronger than normal, and therefore a smaller volume will be required.

Suppose we find that to neutralise 25 c.c. of sodium carbonate we require only 22·6 c.c. of the acid.

---

[1] A rather tedious operation. A good alternative is to use sodium carbonate monohydrate, $Na_2CO_3 \cdot H_2O$ (equivalent 62). The pure substance is obtainable, and it does not deliquesce or effloresce. *Or* we may begin by preparing a normal solution of pure crystallised oxalic acid, $H_2C_2O_4 \cdot 2H_2O$ (equivalent 63), and use this in preparing a normal alkaline solution.

[2] I.e. the process of running one solution from a burette into another solution, so as to find what volume of the first is equivalent to a measured volume of the second.

Now, if we were to take another 22·6 c.c. of acid and add 2·4 c.c. of water, we should have 25 c.c. of an acid solution which would just neutralise 25 c.c. of the carbonate; for although the 22·6 c.c. has been increased to 25, we have not changed the amount of acid present, so that it will neutralise neither more nor less sodium carbonate than it did before.

As our *diluted* acid now neutralises an equal volume of normal sodium carbonate solution, it must itself be normal. Obviously we can normalise the whole of our over-strong acid by adding water to it at the rate of 2·4 c.c. for every 22·6 c.c. of acid.

We can now use our normal acid in a similar way to prepare, say, normal sodium hydroxide. We make a solution of the latter which will be somewhat stronger than normal, titrate normal sulphuric acid against it and proceed as before.

We shall now work out a few typical examples based on volumetric work involving acids and alkalis.

Example 1. *A solution of sodium hydroxide having the specific gravity* 1·32 *contains* 28·8 *per cent. by weight of NaOH. What volume of normal sulphuric acid would be required to neutralise exactly* 1 *litre of such a solution? Camb.*

Specific gravity is 1·32.

$\therefore$ wt. of 1 litre $= 1000 \times 1{\cdot}32$ gm. $= 1320$ gm.

Wt. of NaOH $= \frac{28{\cdot}8}{100} \times 1320 = 380{\cdot}16$ gm.

Equivalent of NaOH $= 23 + 16 + 1 = 40$.

$\therefore$ normal NaOH contains 40 gm./litre.

$\therefore$ 380·16 gm. would make $380{\cdot}16 \div 40 = 9{\cdot}504$ litres of normal solution. This would be neutralised by ***9·504 litres*** of normal sulphuric acid.

Example 2. 1·25 *gm. of anhydrous sodium carbonate is added to* 25 *c.c. of a normal solution of sulphuric acid. Calculate the volume of carbon dioxide set free, if measured at N.T.P. Would the resulting solution be acid or alkaline? Find what volume of deci-normal acid or alkali would be required to neutralise it.*

Equivalent of sodium carbonate, $Na_2CO_3 = \frac{1}{2}(46 + 12 + 48) = 53$.

$\therefore$ 53 gm. would make 1000 c.c. of normal solution.

$\therefore$ 1·25 gm. would make $\frac{1000}{53} \times 1{\cdot}25 = 23{\cdot}60$ c.c.

25 c.c. of normal sulphuric acid would more than neutralise this, the excess of acid being $25 - 23{\cdot}60 = 1{\cdot}40$ c.c. of normal solution $= 14{\cdot}0$ c.c. of deci-normal solution. To neutralise this excess we should require ***14·0 c.c.*** of deci-normal alkali.

Vol. of carbon dioxide.

Equation is $$\underset{\underbrace{46+12+48}_{106}}{Na_2\;\;C\;\;O_3} + H_2SO_4 = Na_2SO_4 + H_2O + \underset{\underbrace{12+32}_{44}}{C\;\;O_2}$$

106 gm. Na_2CO_3 gives 44 gm. $CO_2 = 22{\cdot}4$ litres at N.T.P. (p. 126).

$$\therefore\ 1{\cdot}25 \text{ gm. } Na_2CO_3 \text{ gives } \frac{22{\cdot}4}{106} \times 1{\cdot}25 = 0{\cdot}264 \text{ litre}$$
$$= \mathbf{264\ c.c.}$$

N.B. Note that in titrating a carbonate, we use methyl orange as indicator, *not* litmus. Consider the equation just given. The molecular weight of sulphuric acid is 98, and so neutrality should be recorded when 98 parts by weight of sulphuric acid have been added to 106 parts by weight of sodium carbonate. But in the course of the reaction carbonic acid is produced (from $H_2O + CO_2$), and because this acid reinforces the sulphuric acid, neutrality would be recorded (if litmus were used) *before* 98 parts by weight of sulphuric acid have been added.

We could put matters right by keeping the mixed solutions (acid and carbonate) constantly boiled to expel carbon dioxide, but it is obviously simpler to use an indicator which is not affected by carbonic acid. That is why we use methyl orange.

Example 3. *Hydrogen sulphide was passed through* 200 *c.c. of an aqueous solution of copper sulphate until the chemical action was complete. The precipitate was filtered off and washed, and the combined filtrate and washings titrated with a solution of caustic soda containing* 35 *gm. per litre.* 31 *c.c. of this solution were required. How many grams of crystallised copper sulphate were contained in each litre of the copper sulphate solution? J.M.B.*

Crystallised copper sulphate is $CuSO_4{\cdot}5H_2O$, and we may conveniently write the equation

$$\underset{\underbrace{64+32+64+5(2+16)}_{250}}{Cu\;\;S\;\;O_4\,.\,5H_2\;\;O} + H_2S = CuS + \underset{\underbrace{2+32+64}_{98}}{H_2\;\;S\;\;O_4} + 5H_2O$$

Reaction between caustic soda and sulphuric acid is expressed by the equation

$$\underbrace{\overset{\text{H}_2}{2}+\overset{\text{S}}{32}+\overset{\text{O}_4}{64}}_{98}+\underbrace{\text{2Na O H}}_{}\ldots$$

$$\underbrace{\begin{matrix}H_2 & S & O_4\\ 2+ & 32+ & 64\end{matrix}}_{98} + \underbrace{\begin{matrix}2Na & O & H\\ 2(23+ & 16+ & 1)\end{matrix}}_{80} = Na_2SO_4 + 2H_2O$$

Caustic soda solution contains 35 gm. per litre.

$\therefore$ 31 c.c. contains $\frac{35}{1000} \times 31 = 1{\cdot}085$ gm.

But 80 gm. NaOH neutralises 98 gm. H_2SO_4 (equation).

$\therefore$ 1·085 gm. NaOH neutralises $\frac{98}{80} \times 1{\cdot}085 = 1{\cdot}329$ gm.

But 98 gm. H_2SO_4 corresponds to 250 gm. copper sulphate (equation).

$\therefore$ 1·329 gm. corresponds to $\frac{250}{98} \times 1{\cdot}329 = 3{\cdot}390$.

This was present in 200 c.c.

$\therefore$ each litre contained $3{\cdot}390 \times 5 =$ ***16·95 gm.***

Otherwise thus

The NaOH solution is $\frac{35}{40} = \frac{7}{8}$ths of normal, and 31 c.c. are required.

This is equivalent to $31 \times \frac{7}{8} = 27{\cdot}12$ c.c. of normal solution.

$\therefore$ there is as much sulphuric acid present as would be contained in 27·12 c.c. of normal solution (49 gm. per litre).

This amount $= \frac{49}{1000} \times 27{\cdot}12 = 1{\cdot}329$ gm.

The calculation then proceeds as before.

Example 4. *To* 2·26 *gm. of an ammonium salt were added* 50 *c.c. of normal sodium hydrate solution, and the liquid was boiled until the escaping steam was neutral. Normal sulphuric acid was then added to the liquid until it was neutral. The volume of acid required was* 10 *c.c. Find the percentage of ammonia in the given salt. Scot. L.C.*

10 c.c. of normal sulphuric acid were required.

$\therefore$ as much sodium hydrate is present as would make 10 c.c. of normal solution.

$\therefore$ $50 - 10 = 40$ c.c. have been used to decompose the ammonium salt.

Now 1000 c.c. normal sodium hydrate contain 40 gm.

$\therefore$ 40 c.c. contain $\frac{40}{1000} \times 40 = 1{\cdot}6$ gm.

From equation

$$NH_4X+\underset{\underbrace{23+16+1}_{40}}{Na\ \ O\ \ H}=\underset{\underbrace{14+3}_{17}}{N\ \ H_3}+NaX+H_2O$$

we see that 40 gm. NaOH = 17 gm. NH_3

$\therefore$ 1·6 gm. NaOH $= \frac{17}{40} \times 1{\cdot}6 = 0{\cdot}68$ gm. NH_3

$\therefore$ 2·26 gm. ammonium salt contains 0·68 gm. NH_3

$\therefore$ percentage of ammonia $= \frac{0{\cdot}68}{2{\cdot}26} \times 100 =$ ***30·1.***

Example 5. *What is meant by the gram-equivalent weight of a metal?* 0·50 *gm. of a metal was dissolved in* 25 *c.c. of* 2*N sulphuric acid. Water was added to bring the volume of the solution up to* 100 *c.c. When* 25 *c.c. of the dilute solution were titrated with* $\frac{N}{10}$ *NaOH solution,* 20·8 *c.c. were required for neutralisation. Calculate the gram-equivalent weight of the metal. J.M.B.*

For first part of question see p. 483.

25 c.c. required 20·8 c.c. of $\frac{N}{10}$ NaOH solution.

$\therefore$ 100 c.c. (the whole quantity) would require

$$20{\cdot}8 \times 4 = 83{\cdot}2 \text{ c.c.} = 8{\cdot}32 \text{ c.c. N solution.}$$

$\therefore$ the acid present = 8·32 c.c. N solution.

But the acid present originally = 25 c.c. of 2N solution = 50 c.c. N solution.

$\therefore$ acid used in dissolving metal = 50 − 8·32 = 41·68 c.c. N solution.

Now hydrogen present in 1000 c.c. N solution = 1 gm.

$\therefore$ amount present in 41·68 c.c. = ·04168 gm.

$\therefore$ ·04168 gm. hydrogen is displaced by 0·50 gm. metal.

$\therefore$ 1 gm. is displaced by $\frac{0{\cdot}50}{{\cdot}04168} = 12{\cdot}00$ gm.

I.e. gram-equivalent = ***12·00 gm.***

Potassium Permanganate. Potassium permanganate, $KMnO_4$, is a salt much used in volumetric analysis. It is not used, however, *as* a salt, but as an oxidising agent, and its equivalent weight is therefore calculated as the number of grams which will yield 8 gm. of oxygen in the course of oxidation. (8 *grams* of oxygen because that quantity is equivalent to 1 gm. of hydrogen.)

The easiest way of arriving at the equivalent weight of potassium permanganate is to think of it as splitting up thus:—

$$2KMnO_4 = K_2O + 2MnO + 5O$$

It does not actually do this, but provided that (i) sulphuric acid is present to form the sulphates K_2SO_4 and $MnSO_4$, corresponding to the oxides K_2O and MnO, and that (ii) a reducing agent is present to take up the oxygen (5O in the equation), then $2KMnO_4$ does actually yield 5O. Putting in atomic weights (K=39, Mn=55, O=16), we find that $2(39+55+64)$ or 316 gm. of permanganate yields 80 gm. of oxygen, therefore the equivalent weight of potassium permanganate is 31·6, because this amount would be required to yield 8 gm. of oxygen.

While on the subject of equivalent weights it will be well to consider those of two reducing agents with which potassium permanganate is very often used. These are (i) ferrous salts, (ii) oxalic acid.

(i) As a simple example of a ferrous salt, let us take ferrous sulphate, $FeSO_4$. Here again we are calculating its equivalent, not as a salt, but as a substance capable of combining with oxygen. Let us think of $FeSO_4$ as $FeO{\cdot}SO_3$, because it is the FeO part of the molecule which undergoes oxidation to Fe_2O_3. Then we have $2FeO + O = Fe_2O_3$, or taking the corresponding sulphate, $2FeSO_4$ combines with O. (The equation will be given presently.)

∴ *twice* the molecular weight (in grams) combines with 16 gm. of oxygen.

∴ the molecular weight (in grams) combines with 8 gm. of oxygen, so that *the equivalent weight is numerically equal to the molecular weight, and this result is true for any ferrous salt employed as a reducing agent.*

It is well worth while to build up the equation showing the reaction between potassium permanganate and a ferrous salt.

$$2KMnO_4 \text{ yields } 5O$$

But $2FeSO_4$ is oxidised by *one* O.

∴ $2KMnO_4$ will oxidise $10FeSO_4$, and so we begin our equation with $2KMnO_4 + 10FeSO_4$. Now the potassium, manganese and iron will all be converted into sulphates—the last into ferric sulphate, $Fe_2(SO_4)_3$. The number of 'sulphate' groups required will therefore be 1 for the 2K (becoming K_2SO_4), 2 for the 2Mn (becoming $2MnSO_4$), and 15 for the 10Fe [becoming $5Fe_2(SO_4)_3$], or 18 'sulphate' groups altogether. We are already provided with 10 (in $10FeSO_4$), so we require another 8, which we obtain by inserting $8H_2SO_4$. Our equation is now easily completed:—

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

(ii) Oxalic acid has the formula $H_2C_2O_4$. We may think of it as breaking up, in the presence of an oxidising agent, into $H_2O + CO_2 + CO$ (the CO combining with oxygen). Thus we have

$$H_2C_2O_4 + O = H_2O + 2CO_2$$

Putting in atomic weights we find that $(2 + 24 + 64)$ or 90 gm. of oxalic acid combine with 16 gm. of oxygen, and therefore the equivalent of oxalic acid, $H_2C_2O_4$, is 45 (the amount which combines with 8 gm. of oxygen). Actually, crystallised oxalic acid contains water of crystallisation, its formula being $H_2C_2O_4 \cdot 2H_2O$, and so the equivalent weight is

$$\frac{2 + 24 + 64 + 2(2 + 16)}{2} = 63$$

It is a useful exercise for the student to build up the equation showing the reaction between potassium permanganate and oxalic acid in the presence of sulphuric acid. He should obtain the result

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

We might notice the reaction of permanganate with hydrogen peroxide (as usual, in the presence of sulphuric acid). Here, curiously, the permanganate is reacting with an *oxidising* agent. We may think of hydrogen peroxide, H_2O_2, as $H_2O \cdot O$, and the 'odd' atom is converted into O_2. Reasoning as before, we see that $2KMnO_4$ (yielding 5O) will react with $5H_2O_2$, so we have

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

We often make use of this reaction in finding the strength of a solution of hydrogen peroxide (cf. Example 7 below).

Indicator. The slightest excess of potassium permanganate gives a pink tinge to the solution, so no additional indicator is required.

Example 7. *25 c.c. of hydrogen peroxide solution, prepared from barium peroxide but without further concentration* (p. 159), *was found to be equivalent to 17·86 c.c. of a N/10 solution of potassium permanganate. Find the strength of the peroxide solution.*

From $H_2O_2 = H_2O + O$, we see that 34 gm. of peroxide yields 16 gm. of oxygen.

∴ equivalent is 17, and a N/10 solution would contain 1·7 gm. per litre.

Now 25 c.c. peroxide solution = 17·86 c.c. N/10 permanganate.

$$\therefore \text{ peroxide solution is } \frac{17{\cdot}86}{25} \text{ or } 0{\cdot}714 \text{ of N/10}$$
$$= 0{\cdot}714 \text{ of } 1{\cdot}7 \text{ gm./litre}$$
$$= \mathbf{1{\cdot}214 \text{ gm. per litre.}}$$

Example 8. *10 gm. of a certain ferrous salt was weighed out and dissolved in air-free water, after which the solution was made up to 250 c.c. It was found that 25 c.c. of this solution was oxidised by 28·42 c.c. of a solution of potassium permanganate of strength 5 gm. per litre. Find the percentage of iron in the given ferrous salt.*

Equivalent of potassium permanganate = 31·6.

∴ given solution is 5/31·6 of normal.

But ferrous solution is 'stronger' than permanganate in the ratio 28·42 : 25.

$$\therefore \text{ ferrous solution is } \frac{28{\cdot}42}{25} \times \frac{5}{31{\cdot}6} \text{ of normal.}$$

But a normal ferrous solution would contain 56 gm. of iron per litre (for the equivalent weight of a ferrous salt is numerically equal to the molecular weight).

∴ *this* ferrous solution contains $\frac{28{\cdot}42}{25} \times \frac{5}{31{\cdot}6} \times 56 = 10{\cdot}07$ gm. of *iron* per litre.

But solution contains 50 gm. of the *salt* per litre.

$$\therefore \text{ percentage of iron in the salt} = \frac{10{\cdot}07}{50} \times 100 = \mathbf{20{\cdot}14.}$$

Example 9. It is found that 25 c.c. of a solution of oxalic acid is oxidised by 21·2 c.c. of a solution of potassium permanganate. The former solution contains 6 gm. of the crystallised acid, $H_2C_2O_4{\cdot}2H_2O$ *per litre. Find the strength of the permanganate.*

The equivalent weight of oxalic acid, $H_2C_2O_4{\cdot}2H_2O$, is 63 (p. 491).

∴ the given solution is 6/63 of normal.

But the permanganate solution is 'stronger' than the oxalic acid solution in the ratio 25 : 21·2.

$$\therefore \text{ permanganate solution is } \frac{25}{21{\cdot}2} \times \frac{6}{63} \text{ of normal.}$$

But a normal solution of potassium permanganate would contain 31·6 gm. per litre.

$$\therefore \text{ given solution contains } \frac{25}{21{\cdot}2} \times \frac{6}{63} \times 31{\cdot}6 = \textbf{\textit{3·55 gm. per litre.}}$$

Questions

N.B. *See note in italics*, p. 132

1. Calculate the equivalent weight of each of the following: sulphuric acid, anhydrous sodium carbonate, soda crystals ($Na_2CO_3{\cdot}10H_2O$), hydrochloric acid, sodium bicarbonate, potassium hydroxide.

2. 10 gm. of sodium bicarbonate is heated to constant weight (equation on p. 485). What weight of carbonate would remain, and what volume of deci-normal solution could be prepared from it?

3. You are required to prepare (*a*) 1 litre of normal sulphuric acid; (*b*) 500 c.c. of semi-normal hydrochloric acid; (*c*) 2 litres of semi-normal sodium hydroxide; (*d*) 250 c.c. of deci-normal sodium carbonate. What weight of the pure substance would you require in each case? (*N.B.* The sodium carbonate is supplied in the form of the monohydrate, $Na_2CO_3{\cdot}H_2O$.)

4. What are the normalities of the following solutions:

(i) Sulphuric acid containing 4·9 gm. per litre?
(ii) Sodium hydroxide ,, 8·0 ,, ,,
(iii) Hydrochloric acid ,, 6·0 ,, ,,
(iv) Barium hydroxide ,, 2·75 ,, ,,
(v) Sodium carbonate ,, 10·6 ,, ,,

5. Define the equivalent weight of: (i) an acid; (ii) a base. Write down the equivalent weights of: (1) the substance $KH_3(C_2O_4)_2{\cdot}2H_2O$ as an acid; (2) $Ca(OH)_2$ as a base.

Oxf. (*part*)

6. 21 c.c. of a stronger-than-normal solution of sulphuric acid is required to neutralise 25 c.c. of normal sodium hydroxide. What volume of water must be added to 630 c.c. of the acid to make it normal?

7. 25 c.c. of sodium hydroxide solution is neutralised by 29·2 c.c. of N/2 sulphuric acid. What volume of water must be added to 500 c.c. of the sodium hydroxide solution to make it semi-normal?

8. 25 c.c. of normal sodium hydroxide is neutralised by 20 c.c. of dilute sulphuric acid. Find the strength of the latter solution in grams per litre.

9. Find the strength (in gm. of Na_2CO_3 per litre) of a solution of sodium carbonate, 25 c.c. of which is neutralised by 21·4 c.c. of N/10 hydrochloric acid.

10. 20 c.c. of bench bottle 'hydrochloric acid dilute' is made up to 100 c.c. with water, and it is found that 27·5 c.c. of this diluted solution is required to neutralise 25 c.c. of normal sodium carbonate. Find the strength, in terms of normality, of the bench bottle acid.

11. A solution of sodium bicarbonate (10·08 gm. per litre) is treated with dilute sulphuric acid: 25 c.c. of the alkali required 15 c.c. of the acid. Calculate the normality and concentration of the acid. *Lond.* (*part*)

12. What volume of 1·2N hydrochloric acid will neutralise 20 c.c. of 0·8N caustic soda? *Oxf.* (*part*)

13. In titrating lime-water with standard acid, 50 c.c. of the lime-water required 35 c.c. of 0·06N acid for neutralisation. Calculate the normality of the lime-water, and also its concentration in grams of calcium hydroxide per litre. *Lond.* (*part*)

14. If you were given three unlabelled bottles containing the three common dilute acids, what simple tests would you apply to identify the contents of each bottle?

How would you proceed to find by means of a normal solution of caustic soda, the normality of one of the acid solutions?

If 25 c.c. of any one of the acids required 20 c.c. of the caustic soda for neutralisation, what is the normality of each acid, and what weight per litre of HCl, H_2SO_4 and HNO_3 respectively do the solutions contain? *Lond.*

15. From the equation $Zn + H_2SO_4 = ZnSO_4 + H_2$ calculate the volume of normal sulphuric acid required to dissolve 13·08 gm. of the metal. (Zn=65·4.) *O.C.* (*part*)

16. Given a crystalline specimen of an organic acid (equivalent weight between 70 and 80) and a deci-normal solution of caustic soda, how would you find the exact equivalent weight of the acid? Full experimental details are required.

Oxalic acid is a dibasic acid, formula $C_2H_2O_4{\cdot}xH_2O$. 1·42 gm. of this acid was dissolved in water to give 250 c.c. of solution. 25 c.c. of this solution were neutralised by 20·5 c.c. of 0·11N caustic soda. Calculate x in the formula $C_2H_2O_4{\cdot}xH_2O$.

Scot. L.C.

17. Define: (*a*) the equivalent weight of an acid; (*b*) the basicity of an acid; (*c*) the normal solution of an acid.

A certain carbonate reacts with an acid according to the equation

$$XCO_3 + 2HCl = XCl_2 + H_2O + CO_2$$

If 1 gm. of this carbonate is dissolved in 50 c.c. of normal hydrochloric acid, the remaining acid requires 30 c.c. of normal sodium hydroxide for neutralisation. Find the equivalent weight of the carbonate, and from it deduce the atomic weight of X.

Camb.

18. What do you understand by: (*a*) equivalent weight of an acid; (*b*) the equivalent weight of a base; (*c*) a normal solution? What weights of (i) nitric acid, (ii) sulphuric acid would be required to neutralise 200 c.c. of deci-normal (N/10) potassium hydroxide solution?

A neutral solution is formed when 1·6 gm. of a mixture of chalk and common salt just dissolves in 26·6 c.c. of normal hydrochloric acid. What is the percentage of common salt in the mixture?

Camb.

19. Given pure anhydrous sodium carbonate and concentrated hydrochloric acid (approximately 10N), describe how you would prepare and standardise an approximately deci-normal solution of the acid.

A sample of washing soda ($Na_2CO_3{\cdot}10H_2O$) was exposed to the air for some time, and part of it was converted to the monohydrate ($Na_2CO_3{\cdot}H_2O$). If 2·5 gm. of the mixture were neutralised by 22 c.c. of N hydrochloric acid, calculate the percentage weight of sodium carbonate in the mixture and show that approximately 20 per cent. of the mixture is monohydrate. *Scot. L.C.*

20. What is meant by a normal solution of an acid?

20 ml. of a solution of sulphuric acid containing 98 gm. per litre neutralise 25 ml. of a solution of sodium hydroxide. (*a*) What is the normality of the acid and of the alkali? (*b*) How many grams of sodium hydroxide does a litre contain? (*c*) How much magnesium would a litre of the acid dissolve and what volume of hydrogen, measured at 15° C. and 740 mm. pressure, would be evolved? *Oxf.*

21. Define: (*a*) the equivalent weight of an acid; (*b*) the basicity of an acid. What are the basicity and equivalent weight of sulphurous acid?

A piece of metal weighing 1·1 gm. was added to 75 c.c. of normal hydrochloric acid. The solution was made up to 250 c.c. by adding water. If 25 c.c. of this solution neutralised 27·1 c.c. of a deci-normal solution of sodium hydroxide, calculate the equivalent weight of the metal. *Camb.*

22. It is found that 20 c.c. of a solution of hydrochloric acid are needed to neutralise 25 c.c. of normal sodium hydroxide solution, and that 50 c.c. of the acid will just dissolve 1·75 gm. of a metal X. Calculate the equivalent weight of X.

If the specific heat of X is 0·11, what is its atomic weight?

Write the formulæ for the chloride, nitrate and sulphate of X, using X as the symbol for the metal. *Camb.*

23. 20 ml. of a solution of hydrochloric acid neutralises 25 ml. of a solution of normal sodium hydroxide. 50 ml. of this acid will just dissolve 0·75 gm. of a metal X. Calculate the equivalent weight of X.

If 50 ml. of this acid will neutralise 60 ml. of a solution containing 58·4 gm. per litre of an alkali, what is the equivalent weight of the alkali? *Oxf.*

24. Show what is meant by a normal solution of: (*a*) sulphuric acid; (*b*) caustic soda; (*c*) sodium carbonate.

0·62 gm. of a metallic carbonate was placed in 50 c.c. of normal hydrochloric acid. The resulting solution was heated to expel carbon dioxide and then required 37·6 c.c. of normal sodium hydroxide for neutralisation. Calculate the equivalent of the metal. *Dur.*

25. What do you understand by a *deci-normal* solution of ammonia?

What volume of deci-normal ammonia would be obtained by dissolving 1 litre of the gas (measured at 15° C. and 75 cm. pressure) in water?

What weight of sulphuric acid would be required to neutralise this solution? *Camb.*

26. 5 gm. of copper sulphate, $CuSO_4 \cdot 5H_2O$, are dissolved in water. Calculate: (*a*) the volume of hydrogen sulphide, measured at 15° C. and 740 mm. pressure, which would be required to precipitate the metal completely, and (*b*) the volume of deci-normal sodium hydroxide solution which would be required to neutralise the resulting sulphuric acid. *Camb.*

27. If 25 c.c. hydrogen peroxide solution, acidified, react with 20 c.c. deci-normal permanganate, what is the weight of hydrogen peroxide in 1 litre of the solution? *Oxf.* (*part*)

28. A specimen of crystallised ferrous sulphate, $FeSO_4 \cdot 7H_2O$. originally pure, has become partially oxidised by exposure to air. A solution of it is prepared of strength 26 gm. per litre, and it is found that 25 c.c. of this is oxidised by 21·1 c.c. of N/10 permanganate. Find: (i) the percentage of ferrous iron, and (ii) the percentage of crystallised ferrous sulphate ($FeSO_4 \cdot 7H_2O$) in the specimen.

29. A solution of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) is prepared containing 8 gm. per litre, and it is found that 25 c.c. of this is oxidised by 22·4 c.c. of a solution of potassium permanganate. Find the strength of the latter solution: (i) in terms of normality; (ii) in gm. per litre.

30. State briefly why nitric and hydrochloric acids are not used to acidify potassium permanganate solution.

What is the reaction between acidified potassium permanganate solution and (i) hydrogen peroxide solution, (ii) sulphurous acid?

10 c.c. of hydrogen peroxide solution was diluted with water to 250 c.c., and 25 c.c. of this solution, when acidified with sulphuric acid, reacted with 18 c.c. of deci-normal potassium permanganate solution. Calculate the weight of hydrogen peroxide in a litre of the original solution, and show that its concentration was approximately 10 'volumes.' *Scot. L.C.*

CHAPTER 40

THE ATOM SINCE DALTON

In Chapter 3 we gave an outline of the Atomic Theory put forward by Dalton in 1808. He believed that every element consists of atoms which for any given element are all alike; in particular, they are alike as regards weight. He seems to have thought of atoms as being something like extremely tiny marbles or billiard balls. They had no 'parts'; they could not be taken to pieces nor come to pieces of themselves; and there was no remotest possibility of one kind of atom changing into another.

You will now be very familiar with the meaning of *atomic weight*. Very soon after Dalton had put forward and explained his theory, chemists in England and other countries set to work to ascertain the atomic weights of the various elements. Certain curious features were observed in connection with the numbers thus obtained. In particular, there seemed to be some close connection between the atomic weight of an element and its properties. Finally, in the early years of the present century, evidence began rapidly to accumulate that far from being of simple 'billiard ball' type, the atom is really a very complicated structure made up of only a few different kinds of unit (the protons, neutrons and electrons which will be discussed presently). The structure is held together by tremendous forces, and if for any reason it should disintegrate, an enormous amount of energy is released.

It is this story of what we have called 'The Atom Since Dalton' that (in very brief outline) we shall try to tell in the present chapter.

Prout's Hypothesis. If you look at the table of atomic weights at the end of the book, you will soon notice that, taking O=16 as the standard, a large number of the other values are astonishingly close to *whole numbers*. There are, for instance, C=12·01, F=19·00, N=14·01 and many others—far too many for the peculiarity to be merely the result of chance. A Dr. Prout in 1816 noticed this,[1] and suggested that atoms were not so utterly different from one another as had been supposed, but were all built up from hydrogen atoms. The carbon atom, for instance, would consist of 12 hydrogen atoms closely bound together, the nitrogen atom of 14, and so on. 'Prout's Hypothesis' aroused much interest, but broke down because of such awkward cases as chlorine=35·46 and copper=63·54. In the course of the present chapter we shall see that, during recent years, these awkward cases have been quite satisfactorily explained, and that Prout was really very near the truth.

The Law of Octaves. In 1864 Newlands drew attention to another curious point in which atomic weights were again closely concerned. Beginning with lithium, we write down the elements in order of increasing atomic weight—i.e. lithium (7), beryllium (9), boron (11), carbon (12) and so on. After writing down seven elements we come to sodium, *an element in many respects like lithium*, then to magnesium, *which somewhat resembles beryllium*, and so on. It is very like going up the scale on the piano. After seven notes we find that the series begins, to a certain extent, to repeat itself; and in fact Newlands called his discovery 'The Law of Octaves.' The first two chemical octaves would be

Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl

Even with our elementary knowledge of chemistry we can see certain resemblances. Fluorine and chlorine, for instance, members of the halogen family, are an octave apart, so are carbon and silicon, with their tendency to form 'chain' compounds; and so are nitrogen and phosphorus, which form many compounds of similar composition—e.g. N_2O_5, P_2O_5; HNO_3 (nitric acid), HPO_3 (phosphoric acid); NH_3 (ammonia), PH_3 (phosphine), and so on.

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[1] I.e. not the actual examples (and values) just given, but the general 'whole number' tendency. In 1816 the values accepted for the atomic weights were very inaccurate. In fact, it was largely to test Prout's hypothesis that chemists began to make really accurate atomic weight determinations.

The Periodic System. A few years later (in 1869), Newlands' discovery was greatly extended by the Russian chemist Mendeléeff. He showed that octaves alone would not meet the situation, but that in some cases it was necessary to write down seventeen elements (instead of seven) before a repetition of properties was encountered. Thus, counting in order of atomic weights, seventeen[1] elements from chlorine we come to bromine, and seventeen[1] elements beyond that we come to iodine. Part of Mendeléeff's 'Periodic Table' is given below, elements discovered since 1869 being shown in fainter type.

GROUP

[redacted]

0	I	II	III	IV	V	VI	VII	VIII
	H							
He	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**	
Ne	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	
A	**K**	**Ca**	Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe Co Ni**
	Cu	**Zn**	Ga	Ge	**As**	**Se**	**Br**	
Kr	**Rb**	**Sr**	**Yt**	**Zr**	**Nb**	**Mo**	Ma	**Ru Rh Pd**
	Ag	**Cd**	**In**	**Sn**	**Sb**	**Te**	**I**	

In some cases he found that *using the atomic weights accepted at that time*, the elements concerned would not fit into his table. Indium, for instance, was believed to have an atomic weight of 76, which would place it between arsenic (75) and selenium (79). But between these two elements there was no vacant space.

Now the number 76 had been accepted because the *equivalent* was certainly 38, and it had been assumed (on rather flimsy evidence) that the valency was 2.

$$\text{Atomic wt.} = \text{Equiv.} \times \text{Valency (p. 64)} = 38 \times 2 = 76.$$

Mendeléeff suggested that the valency might be 3, not 2. That would give an atomic weight of 38 × 3 = 114, and then the element would fit very conveniently into an otherwise vacant space between cadmium (112) and tin (119).

Naturally the question of the atomic weight of indium now received special attention. The specific heat of the element was found to be 0·057, indicating that the atomic weight was

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[1] Really 18, but the 'Group 0' elements were not known in 1869.

roughly $6{\cdot}3 \div 0{\cdot}057 = 111$ (Dulong and Petit's Law, p. 66). As the choice is between 76 and 114, this rough value causes us to choose the latter number. Later, further evidence was obtained that indium is indeed trivalent. This is only one of a number of cases in which Mendcléeff's table resulted in the correction of faulty atomic weight values.

We have referred to the fact that in 1869 a number of elements still awaited discovery. It is interesting to consider a typical example—the element now known as germanium (Ge), below silicon in Group IV. Mendeléeff gave it the provisional name eka-silicon (Es). Its atomic weight would obviously be a little less than that of arsenic (75), but from a consideration of the properties of neighbouring elements in the Table, Mendeléeff was able to forecast other properties. He made his forecast in 1871, and the missing element was discovered fifteen years later. Here are a few of the properties forecast for eka-silicon compared with the actual properties of germanium.

Eka-silicon	*Germanium*
Atomic weight about 72	Atomic weight 72·6
Density about 5·5	Density 5·47
Colour, dirty grey	Colour, greyish white
Would yield a white oxide, EsO_2	Yields a white oxide, GeO_2
Its chloride, $EsCl_4$, will be a liquid of sp. gr. about 1·9 and boiling below 100° C.	Chloride, $GeCl_4$, is a liquid of sp. gr. 1·887 and boiling point 86·5° C.

Mendeléeff also made brilliant predictions relating to other elements not known in 1869 but discovered later.

But there were failures too. Thus if arranged in accordance with *properties*, iodine must be put in the same group (VII) as bromine, and tellurium in the same one (VI) as selenium. As tellurium would then precede iodine, it should have a lower atomic weight, but the accepted values were the other way about!

'No doubt an error of a unit or two in the accepted values,' it was thought. Most careful redeterminations were made, but the atomic weights finally assigned, only confirmed the 'wrong' order already mentioned.

Before passing on, we must notice just one other feature in connection with the periodic table—the fairly regular change in *valency*. Take the 'sodium' line. The valency of sodium is 1 (e.g. NaCl), of magnesium 2 ($MgCl_2$), of aluminium 3 (Al_2O_3), of silicon 4 (SiO_2 and SiH_4). Phosphorus sometimes has a valency of 5 (P_2O_5, PCl_5), sulphur of 6 (SO_3) and chlorine occasionally of 7 (Cl_2O_7). The elements of 'Group 0' were not discovered till about the end of the century. It was then found that they fitted into the table very well *with a valency of* 0—they simply declined to combine with any other element whatever. The reason why we have specially touched on this question of valency will appear later.

Biographical Note. Dmitri Ivanovitch Mendeléeff was born in 1834 at Tobolsk in Siberia, the youngest of a family of fourteen children. A friend of the family, a political exile named Basargin, was keenly interested in science, and at an early age Dmitri caught the enthusiasm. At Tobolsk, however, educational facilities were very meagre, and the boy's prospects must have seemed still more hopeless when his father died, Dmitri being then only thirteen. His mother, however, was a very remarkable woman, and she determined that he should have his chance. Accordingly, a year or two later, she undertook with him the long 1200-mile walk to St. Petersburg (now Leningrad)—there was at that time no trans-Siberian railway—'spending thus her last resources and strength' as her son wrote years afterwards. At St. Petersburg, because of his Siberian origin, the authorities would not admit the boy to college, so the two pushed on to Moscow, where they were successful; but a few months later the mother died. The youth now had his chance, and made such good use of it that long before his death in 1907 he had attained a high place among the world's great scientists.

Atomic Structure. Looking back at Prout's hypothesis—discredited as it was—at Newlands' Law of Octaves and at the very curious relationships of Mendeléeff's table, we cannot resist a strong feeling that there must be an explanation somewhere if only it could be found. The first hint of an explanation came in 1898 when Mme Curie obtained the bromide of a new element, *radium*. The element itself was not isolated till 1911.

Radium is an element of atomic weight 226. One of the puzzling things about it is, that it is always hotter than its surroundings—always, therefore, giving out heat. Now a *compound* might give out heat in the process of decomposition (though more often it absorbs heat). But how could an *element* give out heat? Before long the astonishing discovery was made that *radium is all the time undergoing decomposition* (the word 'disintegration,' however, is generally used in this connection). As it does so it discharges 'alpha-particles' into the surrounding space with a velocity which averages about one-twentieth that of light, or say 20,000 times that of a rifle-bullet. These α-particles have been found to be slightly modified atoms of helium,[1] and it is the impact of the α-particles on the surrounding medium that is the cause of the continual production of heat. There is some connection, then, between the atom of radium and the atom of helium. We begin to think of Prout.

Sir Ernest (afterwards Lord) Rutherford thought interesting results might be obtained if he used these α-particles to *bombard* the atoms of some other substance. We must pass over the wonderful story of how a method was discovered of photographing the track of the projectile (α-particle) both before and after it hit the target (i.e. one of the atoms being bombarded). The point is, that for every case in which the photograph indicated a 'head-on collision' (the track suddenly turning off at a sharp angle), there were hundreds in which the α-particle had evidently passed *clean through the atom*, for the path showed no deviation. From these results and from other considerations, Rutherford came to the conclusion that the atoms he was bombarding consisted of a central nucleus surrounded by tiny bodies called electrons, very much as the solar system consists of a central sun surrounded by planets moving in various orbits. The size of the atom is the size of the *system*, and this is enormously greater than that of the central nucleus. If the latter is represented by a cricket ball, the diameter of the system might be about a mile. An atom, in fact, consists almost entirely of empty space, and it is not surprising that Rutherford only rarely secured a more or less 'head-on' collision—his α-particles nearly always shot right through the atom instead of hitting (or going very near) the central nucleus.

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[1] I.e. atoms of helium *minus* the electrons (p. 505).

If we think for a moment, we realise that there is a serious objection to the α-particle considered as a projectile. It is *positively charged.* Now the nucleus is also positively charged, and we know from our studies in electricity that 'like' charges repel one another. It must often happen, then, that an α-particle which would give the nucleus at least a glancing blow, so to speak, is pushed away by this repulsive force and misses it altogether. Rutherford would very much have preferred uncharged particles for his projectiles if he could have obtained them.

Later, such particles really were obtained. In 1930 some workers in Germany were using α-particles to bombard certain elements of low atomic weight (lithium, boron and beryllium). The bombardment caused these elements to give out something of a very puzzling character. It took about two years to settle what this 'something' was, and it turned out to be a collection of particles exactly resembling α-particles, except that they were *uncharged.* They were given the name *neutrons.*

And now, piecing together the results of years of hard work by scientists of many nationalities, it became possible to understand a great deal more of the structure of the atom. Let us begin with the simplest atom, that of hydrogen. Its nucleus consists of a positively charged particle known as a *proton,* while revolving about it is a single electron, whose negative charge exactly balances the positive charge on the proton, causing the atom as a whole to be neutral.

The next heavier atom, helium, has *two* electrons revolving about its nucleus, the latter containing two protons whose charges balance the negative charges on the two electrons. But the atomic weight of helium is 4, not 2. The extra two units of weight are contributed by two neutrons (a neutron has practically the same weight as a proton, i.e. the same weight as a hydrogen atom; for the weight of the electron is so small that for most purposes we may neglect it). Thus the helium atom may be represented somewhat as in fig. 40/1, where the shaded circles in the centre represent neutrons, and the white circles represent protons. (It is worth noting that if the 'orbit' of the electrons were drawn truly to scale in comparison with the nucleus, it would have a diameter of about 50 yards!) Protons, neutrons and electrons are *the same for all elements.*

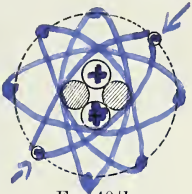

FIG. 40/1
The helium atom
(diagrammatic only)

Proceeding in order of atomic weight, lithium (atomic weight 7) would have three electrons, beryllium (atomic weight 9) would have four and so on, until we come to one of the heaviest atoms of all, that of uranium (atomic weight 238), with 92 electrons. It seems, then, that all atoms are built up of the same fundamental parts, protons, neutrons and electrons.[1] The number of protons is always equal to the number of electrons, the positive charges on the one cancelling out the negative charges on the other. Thus uranium with 92 electrons will have 92 protons. The total weight of 238 units is made up by the addition of 238 - 92 = 146 neutrons. The number of electrons in an atom is known as the *atomic number.* For instance, the atomic number of hydrogen is 1, of helium 2 and so on, that of uranium being 92.

As the nucleus usually contains many positively charged particles (protons) in very close proximity to one another, the question at once arises—How does it hold together? (for we would expect positively charged bodies to repel one another).

We do not really know the answer to this question, but apparently when bodies are *very* close together—as the protons are in the nucleus—some special force of attraction comes into play, which more than balances the force of repulsion due to similar charges. But when the nucleus becomes very large—as in the case of radium—some of the protons are pushed farther apart by the intervening protons and neutrons. The 'close together' force, whatever it is, may become less than the electrical forces of repulsion, and the nucleus may break up. That is why the very heaviest atoms (radium, uranium, etc.) are radioactive.

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[1] These three fundamental parts could perhaps be reduced to two, for there is some evidence that the neutron consists of a proton firmly combined with an electron. On the other hand, there are certain atomic constituents (e.g. the positron) which we have omitted as not being essential to our simplified scheme.

The chemical properties of an atom depend *not* on the nucleus, *but on the number and arrangement of its electrons.* Thus if for some reason extra neutrons enter the nucleus of an atom, we shall have an increase of atomic weight without any change in properties. For instance, while all atoms of chlorine contain 17 protons in the nucleus, electrically balanced by 17 surrounding electrons, the nucleus in some cases contains 18 neutrons, making the atomic weight up to $17+18=35$, while in others it contains 20, making the atomic weight $17+20=37$. As a result there are really two kinds of chlorine, with identical chemical properties because they have the same electronic structure, but differing in atomic weight. The two kinds are known as *isotopes,* and ordinary chlorine contains these in such proportions as to yield a mixture having an atomic weight of 35·46.

In a number of cases the atoms are all of one kind—i.e. there are no isotopic forms—and we then get the 'whole number' atomic weight that attracted the notice of Prout. Iodine (53 protons, 74 neutrons, atomic weight 127) is an example. More often there are isotopes. Tellurium has as many as eight. In all of them there are 52 protons, but the number of neutrons ranges from 68 to 78, giving atomic weights ranging from 120 to 130. It happens that the mixture contains a high proportion of the heavier atoms, giving the average value of 127·6 which Mendeléeff found so disturbing because it was higher than the atomic weight of iodine. If he had been able to use atomic numbers instead of atomic weights, he would have had a perfect table.

In the case of hydrogen, though the nucleus usually consists of only a single proton, there may be a neutron present as well, or occasionally two neutrons. In the former case we have a hydrogen whose *atom* weighs 2 units. It is known as deuterium (D). Ordinary hydrogen contains about 1 part in 7000 of deuterium, and water contains a corresponding proportion of deuterium oxide, D_2O. By a process depending on electrolysis, this can be isolated from ordinary water, giving 'heavy water.' This has a density of 1·108. It boils at

101·4°, freezes at 3·8° and is used in connection with the atomic pile.

We may mention here that *radioactive* isotopes of most of the elements can be prepared, i.e. isotopes which, like radium, emit electrons, or α-particles, or both. These electrons, etc., produce certain effects which enable them to be counted by an instrument known as a Geiger counter, and the result is that the presence of the smallest trace of a radioactive element can be detected. This fact is giving enormous assistance to the work of research. To take just one example. A farmer often uses superphosphate as a fertilizer. Do the plants take it up almost immediately, or does it become effective only after a long period? Is it taken up by all crops?

To solve such problems, the scientist prepares some superphosphate from *radioactive* phosphorus, and mixes a little of this special preparation with ordinary superphosphate. It is important to understand that the radioactive substance will affect the plant is exactly the same way as the 'ordinary' material. The only difference is that the radioactive substance can be detected.

Working in this way—and cutting up his plant at the end of the experiment—the scientist can find out how long it takes for superphosphate to take effect, how much goes to the root, how much to the stem and so on. For an obvious reason, the radioactive phosphorus is known as a *tracer element*, and the example given is only one of hundreds in which tracer elements have been used.

Valency. We must now consider the relation of electrons to the subject of valency. We have seen that the electrons move in orbits (possibly these orbits are really 'shells,' but that will not affect our discussion). The first orbit may contain 1 electron (as in the case of hydrogen) or 2 (the case of helium). Lithium has 3 electrons, 2 in the first or inner orbit and 1 in the second. After this the elements in order (beryllium, boron, carbon, etc.) keep adding 1 electron to the second orbit until neon is reached with 10 electrons, of which 2 are in the inner orbit, as shown in fig. 40/2.

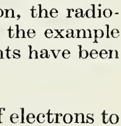


FIG. 40/2

It seems that 8 electrons in the second orbit form a very stable arrangement—one not easily disturbed (similarly for 2 electrons in the first orbit). After the 2–8 system is completed a third orbit begins to be built up. Thus we have Ne 2.8.0, Na 2.8.1, Mg 2.8.2, Al 2.8.3, Si 2.8.4, P 2.8.5, S 2.8.6, and Cl 2.8.7 (i.e. 2 electrons in the inner orbit, 8 in the second, and 7 in the third).

Now suppose an atom of sodium meets one of chlorine. The sodium atom (2.8.1) says (we may imagine), 'I should feel much steadier without this outer electron.' The chlorine atom (2.8.7) replies, 'And *I* should be much steadier with an extra one. It would just make up my outer orbit to 8.' So the sodium atom loses an electron to the chlorine, and with the formation of sodium chloride both achieve stability. Considering the outer orbit only, we may write

$$\mathrm{Na}\cdot + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}\!: \rightarrow \Big[\mathrm{Na}\Big]\Big[:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}:\Big] \quad \text{or} \quad \mathrm{Na}^{+}\mathrm{Cl}^{-}$$

The *plus* sign is attached to 'Na,' because as the sodium atom was formerly neutral and has lost a *negative* electron, it will now be electro-positive. Similarly, the chlorine atom will be electro-negative. These electrical characters become obvious when a solution of sodium chloride is electrolysed.

You can easily work out other cases for yourself; e.g. if calcium (2.8.8.2) and chlorine (2.8.7) meet, there will be stability for both if *one* atom of calcium loses *two* electrons, and *two* atoms of chlorine each gain *one*

$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}\cdot + \cdot\,\mathrm{Ca}\,\cdot + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}\!: \rightarrow \Big[:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}:\Big]\Big[\mathrm{Ca}\Big]\Big[:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}:\Big] \quad \text{or} \quad \mathrm{Ca}^{++}\mathrm{Cl}_2^{=}$$

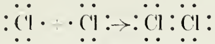
So 1 atom of calcium combines with 2 of chlorine, forming calcium chloride, $CaCl_2$. Similarly, with oxygen (2.6) we have

$$\mathrm{Ca}\,: + \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}\!: \rightarrow \Big[\mathrm{Ca}\Big]\Big[:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:\Big] \quad \text{or} \quad \mathrm{Ca}^{++}\mathrm{O}^{=}$$

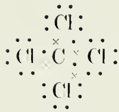
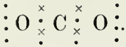
Thus while sodium behaves as a univalent element, calcium behaves as a divalent element and so on. We begin to see why the valency steadily advances as we pass along the horizontal lines of the Periodic Table. We can also see why helium (2.0), neon (2.8), argon (2.8.8), etc., already stable, have no 'inducement,' so to speak, to combine with other elements. Their valency is zero.

In cases like those just mentioned, where atoms combine by the *transfer* of one or more electrons from one atom to the other, they are said to be united by *electrovalent* or *polar* bonds, the compound being known as a *polar* compound.

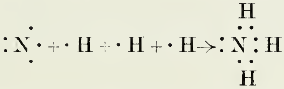
While on this subject of the electrical nature of valency, let us consider a group of cases in which the stable 'octet' of electrons is secured not by transfer, but by *sharing*. Thus, when two chlorine atoms combine to form Cl_2, we have



$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}\cdot + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \rightarrow :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:$$

Here two electrons are *shared*, with the result that each chlorine atom in 'Cl_2' is surrounded by 8 electrons, and we have stability. The two atoms may, of course, be different, as when carbon $\times\underset{\times}{\overset{\times}{C}}\times$ combines with chlorine $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}\cdot$, giving carbon tetrachloride  $\begin{array}{c} :\overset{\cdot\cdot}{Cl}: \\ :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}\,\overset{\times}{\underset{\times}{\cdot C \cdot}}\,\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \\ :\underset{\cdot\cdot}{Cl}: \end{array}$ or with oxygen $:\underset{\cdot}{\overset{\cdot}{O}}:$, giving carbon dioxide  $\underset{\cdot}{\overset{\cdot}{:O}}\,\underset{\times}{\overset{\times}{:}}\,C\,\underset{\times}{\overset{\times}{:}}\,\underset{\cdot}{\overset{\cdot}{O:}}$. (The crosses and dots are used only for clearness, the electrons are of course all alike.) Atoms joined in the way just described, i.e. by the *sharing* of electrons, are said to be united by *co-valent* or *non-polar* bonds.

The case of ammonia, NH_3, is curious. In its formation, nitrogen (2.5) shares 3 pairs of electrons with hydrogen



$$:\underset{\cdot}{\overset{\cdot}{N}}\cdot + \cdot H + \cdot H + \cdot H \rightarrow :\underset{\underset{H}{\cdot\cdot}}{\overset{\overset{H}{\cdot\cdot}}{N}}:H$$

There is evidently the possibility of some further sharing, and it is this which gives rise to the ammonium compounds, such as the chloride, NH_4Cl.

Even in this very brief survey we can see that the modern theory of atomic structure throws a flood of light on the path trodden by the nineteenth-century chemists. But it lights up the path ahead as well as that which lies behind. It shows that, since all atoms have the same constituent parts—protons, neutrons and electrons—it should not be impossible to turn one element into another. Let us consider this point.

Going back a little way, we saw that, considered as a projectile for bombarding atomic nuclei, the neutron seems far more promising than the α-particle, because, being uncharged, it will not be repelled by the positively charged nucleus. Neutrons were therefore used in the way we are discussing, and the results first noticed, though interesting enough, were very much what we should expect. Sometimes one or more of the particles simply buried themselves in the nucleus, producing a heavier isotope of the element that was being bombarded (not a different *element*—that would require a change in the *electronic* structure). Sometimes one or two protons and electrons would be dislodged, giving rise to *atoms of a new element* of slightly lower atomic weight. In short, the atom might receive a little addition, or it might have a bit chipped off; but it was never completely broken.

But in January 1939 something quite different was observed. As a result of bombarding uranium with neutrons, atoms of an isotope of *barium* made their appearance, along with other products. Now the atomic weight of uranium is 238, while that of barium is 137. Evidently the atoms of uranium must have been split into (very roughly) equal halves.

Here, then, we have a clear case of the conversion of one element into another (uranium into barium), in addition to an earlier one noted (radium into helium), and the 'elements of slightly lower atomic weight' mentioned just above. Actually the list of conversions is very much longer than this, but enough has been said to show that the various elements are by no means so fundamentally different as Dalton supposed.

Atomic Energy. We have just noted the breaking up—the *fission* as it is called—of the atom of uranium. It would give a better idea of what happened if we had described it as *exploding*, for the portions into which the atom was broken up flew apart with incredible velocity. In other words, a large amount of kinetic energy made its appearance. Still, only a comparatively few atoms would undergo fission, so, though the energy released was very large compared with the tiny amount of matter involved, it would certainly be very small in itself.

But there is another point of great importance. When uranium atoms are broken up by neutrons, *a few other neutrons are set free.* Might not these neutrons cause other uranium atoms to undergo fission, producing fresh neutrons, which in turn would produce fission in still other atoms and so on? In short, might we not have a *chain reaction,* causing fission—and therefore the release of energy—on a large scale?

What we are suggesting is something like the lighting of a fire. By means of a match we supply heat to a small portion of the fuel. This takes fire, probably giving out more heat than was first supplied by the match. This larger amount of heat can set fire to a larger amount of fuel, and so the process goes forward on an ever-increasing scale. The fire 'spreads.'

But we know that this does not always happen. Some of the heat supplied by our lighted match probably escapes ineffectively into the air. Some may be absorbed by damp fuel in the neighbourhood, which it fails to set on fire, and so on; the fire will not 'catch.' In the same way, it by no means follows that when some atoms in a quantity of uranium undergo fission, a chain reaction will result. However, without going into details, we may say that it *is* possible to arrange for a chain reaction to be set up in a mass of uranium.[1] Energy may be released with extreme speed, giving us a bomb which could destroy a city. In the *atomic pile,* however, conditions are so arranged (by methods which include the slowing down of the neutrons with blocks of pure graphite), that this energy is released at a comparatively slow and regulated speed, giving us a useful source of power to replace, at least in part, energy that has hitherto been obtained from coal and oil.

The fisherman in the old story released, from a sealed vase, a mighty smoke genie who had been imprisoned there for centuries. By a simple ruse he induced the genie to re-enter the vase, and so avoided destruction. In these later days our scientists, probing into the core of the atom, have released a genie infinitely more powerful, but to us no 'as you were' is possible. It may destroy man's fairest works and produce death and misery on a scale never hitherto imagined. On the other hand, it may carry his burdens and take from him every anxiety connected with his dwindling sources of power. Everything depends on whether he can solve the most difficult problem that has presented itself in all his history—the problem of how to live at peace with his neighbours.

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[1] Note that while energy is released by the *splitting* of heavy atoms (e.g. uranium), it is also released by the combination of light ones (e.g. hydrogen), as when two atoms of 'heavy hydrogen' or deuterium (p. 506) combine to form an atom of helium. The latter reaction is believed to be the source of the vast amount of energy constantly emitted by the sun, and it is also operative in the terrible hydrogen bomb. It seems likely that before long it will be found possible to 'harness' this energy for industrial purposes.

Questions

1. Write a short account of the Periodic System, and show how it stimulated work connected with the determination of atomic weights, and with the discovery of new elements.

2. For many years the elements iodine and tellurium were irregular in their relation to the Periodic System. Explain the nature of the irregularity and show how it was finally accounted for.

3. Give your reasons for believing or disbelieving that atoms are indivisible and can neither be created nor destroyed.

J.M.B. Alt. (*part*)

4. Explain simply the difference between *electro-valency* and *covalency*. Of which of these two types of valency is ammonia an example?

Give a simple electronic diagram to show the essential structure of the ammonia molecule.

Also give diagrams to explain why: (*a*) a sodium atom is electrically neutral; (*b*) a sodium ion is positively charged. (Give keys to your diagrams to explain the symbols you use.)

J.M.B. Alt.

APPENDIX I

REVISION NOTES

(*a*) PREPARATION AND PROPERTIES OF GASES

General Remarks

(i) *Collection.* Of the gases dealt with below, oxygen, hydrogen, nitrogen, nitric oxide and the four compounds of carbon may all be collected over cold water.

Chlorine, hydrogen sulphide and nitrous oxide may be collected over *hot* water. Ammonia (a light gas) is collected by displacing air downwards, while hydrogen chloride, sulphur dioxide and nitrogen peroxide are collected by displacing it upwards.

(ii) *Drying.* In most cases the gas may be dried by passing it through a U-tube containing either pieces of anhydrous calcium chloride or pumice stone moistened with concentrated sulphuric acid.

Ethylene and acetylene are absorbed by sulphuric acid, but may be dried with calcium chloride. The same applies to nitrogen dioxide. Ammonia is dried with quicklime or solid caustic soda, and hydrogen sulphide with phosphorus pentoxide.

(iii) Remember that the chief *physical* properties of a gas are colour, smell, (taste), heaviness (especially in comparison with air), solubility in water and whether easily liquefied or not. (It is convenient to remember that the gases which are easily dissolved are in most cases easily liquefied, and vice versa.)

The density of air relative to hydrogen is 14·4, and the density of any pure gas=(mol. wt.) ÷ 2. Thus we can easily find whether any gas is heavier or lighter than air.

E.g. ammonia (NH_3). Mol. wt ÷ 2 = 17 ÷ 2 = 8·5. This is less than 14·4.

∴ ammonia is lighter than air.

Chlorine (Cl_2). Mol. wt. ÷ 2 = 71 ÷ 2 = 35·5.

∴ chlorine is about 2½ times as heavy as air.

(iv) The list of properties given in the following summary is far from complete, but the more characteristic ones have been included, and also those most likely to be forgotten or confused.

Oxygen. Heat potassium chlorate mixed with about a quarter its weight of manganese dioxide:—

$$2KClO_3 = 2KCl + 3O_2$$

Test. Re-ignites glowing splint.

Distinguished from nitrous oxide by the fact that it forms brown fumes with nitric oxide.

Hydrogen. Add dilute sulphuric (or hydrochloric) acid to zinc

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

Test. Burns with a slight 'pop' (except when very free from admixture with air).

Distinguished from carbon monoxide by the fact that if lime-water is added after burning, it is not turned milky.

Other Properties. Reducing agent, e.g. when passed over copper oxide, copper is produced

$$CuO + H_2 = Cu + H_2O$$

Nitrogen. Nitrogen (containing, however, about 1 per cent. argon) may be obtained from air by removing the oxygen (using phosphorus, damp iron filings, etc.).

Nitrogen free from argon may be made by heating a solution of sodium nitrite and ammonium chloride:—

$$NaNO_2 + NH_4Cl = NaCl + 2H_2O + N_2$$

Tests. Chiefly of a negative character—no effect on litmus, lime-water, etc.; neither burns nor supports combustion. Density relative to hydrogen = 14.

Carbon dioxide. Add dilute hydrochloric acid to marble chips

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

Test. Turns lime-water milky.

Other Properties. Faintly acid to litmus, forming carbonic acid

$$CO_2 + H_2O = H_2CO_3$$

When passed over heated carbon it is reduced to carbon monoxide

$$CO_2 + C = 2CO$$

Carbon monoxide. Heat oxalic acid with concentrated sulphuric acid:—

$$H_2C_2O_4 = H_2O + CO_2 + CO$$

Before collecting, pass the mixed gases through a strong solution of caustic soda to absorb the carbon dioxide:—

$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$

Test. Burns with a blue flame, and afterwards turns lime-water milky.

Methane. Heat a mixture of sodium acetate and soda lime in a copper flask:—

$$CH_3\boxed{\cdot COONa + NaO}H = Na_2CO_3 + CH_4$$

Test. Burns with slightly luminous flame, forming carbon dioxide and water ($CH_4 + 2O_2 = CO_2 + 2H_2O$).

Density relative to hydrogen = 8.

Other Properties. Forms only *substitution* products with halogens, etc. E.g.

$$CH_4 + Cl_2 = CH_3Cl + HCl$$

Ethylene. Heat alcohol with sulphuric acid at a temperature of 165° C.

$$C_2H_6O = H_2O + C_2H_4$$

Test. Burns with a smoky, luminous flame, forming carbon dioxide and water, together with some free carbon:—

$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$$

Density relative to hydrogen = 14.

Other Properties. Forms *addition* products with halogens, etc. E.g.

$$C_2H_4 + Cl_2 = C_2H_4Cl_2$$

Acetylene. Add water to calcium carbide:—

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

Test. Gives a red precipitate ('cuprous acetylide') when passed into a solution of cuprous chloride in ammonia.

Other Properties. Burns with very bright, smoky flame, forming carbon dioxide and water together with free carbon:—

$$2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O$$

Forms *addition* products with halogens, etc.—e.g.

$$C_2H_2 + 2Cl_2 = C_2H_2Cl_4$$

Hydrogen sulphide. Add dilute sulphuric or hydrochloric acid to lumps of ferrous sulphide:—

$$FeS + H_2SO_4 = FeSO_4 + H_2S$$
$$FeS + 2HCl = FeCl_2 + H_2S$$

If the gas is required *dry* it must not be passed through concentrated sulphuric acid (which reacts with it). Calcium chloride also reacts, but only slowly, and so is often used. Strictly speaking, phosphorus pentoxide (P_2O_5) should be employed.

Test. Characteristic smell of bad eggs. Blackens lead acetate paper.

Other Properties. Last result is due to formation of lead sulphide. Similarly copper sulphide is precipitated from a solution of copper sulphate:—

$$CuSO_4 + H_2S = CuS + H_2SO_4$$

A sulphide is *not* precipitated, however, from a solution of ferric chloride, but ferrous chloride remains in solution:—

$$2FeCl_3 + H_2S = 2HCl + S + 2FeCl_2$$

It reacts with sulphur dioxide:—

$$SO_2 + 2H_2S = 2H_2O + 3S$$

and with chlorine:—

$$Cl_2 + H_2S = 2HCl + S$$

Sulphur dioxide. Heat copper with concentrated sulphuric acid:—

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2$$

Smell of burning sulphur *and* decolorises potassium permanganate. (The latter test must be confirmed by the smell, because other reducing agents, e.g. hydrogen sulphide, will decolorise permanganate.)

Other Properties. With water it forms a weak acid, sulphurous acid, from which the *sulphites* are derived:—

$$H_2O + SO_2 = H_2SO_3$$

If passed into sodium hydroxide solution, sodium sulphite is formed (in solution). If excess of the gas is used, sodium hydrogen sulphite is formed:—

$$2NaOH + SO_2 = Na_2SO_3 + H_2O$$
$$NaOH + SO_2 = NaHSO_3$$

Chlorine in solution is reduced to hydrogen chloride:—

$$Cl_2 + SO_2 + 2H_2O = H_2SO_4 + 2HCl$$

Nitrogen dioxide (in presence of water) is reduced to nitric oxide:—

$$H_2O + SO_2 = H_2SO_3$$
$$H_2SO_3 + NO_2 = H_2SO_4 + NO$$

(cf. lead chamber process).

For reaction with hydrogen sulphide see p. 284.

Hydrogen chloride. Heat common salt with *slightly* diluted sulphuric acid:—

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$

Test. Characteristic smell. Steamy fumes produced on breathing across the mouth of the gas-jar or test-tube. Forms dense white fumes with ammonia.

Other Properties. Extremely soluble in water, forming hydrochloric acid. With bases the latter gives chlorides, e.g.

$$NaOH + HCl = NaCl + H_2O$$

With oxidising agents it gives chlorine, e.g.

$$Pb_3O_4 + 8HCl = 4H_2O + 3PbCl_2 + Cl_2$$

(see also next equation).

Chlorine. Heat manganese dioxide with concentrated hydrochloric acid:—

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$$

Test. Characteristic smell. Greenish colour. Bleaches litmus.

Other Properties. 1. Combines directly with hydrogen, and reacts vigorously with many compounds containing hydrogen, e.g.

(i) Hot turpentine takes fire in the gas

$$C_{10}H_{16} + 8Cl_2 = 16HCl + 10C$$

(ii) With water, in presence of sunlight, it gives hydrochloric acid and hypochlorous acid, the latter then giving off oxygen:—

$$H_2O + Cl_2 = HCl + HClO$$
$$2HClO = 2HCl + O_2$$

(iii) Reactions with hydrogen sulphide, methane and with solution of sulphur dioxide, already given.

(iv) Liberates nitrogen from ammonia:—

$$2NH_3 + 3Cl_2 = 6HCl + N_2$$
$$(\text{then } HCl + NH_3 = NH_4Cl)$$

2. Readily forms chloride with phosphorus, antimony, copper (in Dutch metal) and many other elements.

3. Displaces bromine and iodine from solutions of potassium bromide and iodide respectively.

4. Combines with unsaturated compounds, e.g.

$$CO + Cl_2 = COCl_2$$
$$C_2H_4 + Cl_2 = C_2H_4Cl_2$$
$$C_2H_2 + 2Cl_2 = C_2H_2Cl_4$$

Ammonia. Heat ammonium chloride with slaked lime:—

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2H_2O + 2NH_3$$

Test. Characteristic smell. Turns damp litmus paper blue.

N.B. Ammonia reacts with calcium chloride, sulphuric acid and phosphorus pentoxide. It is dried by passing it through a U-tube, or tower, containing small lumps of *quicklime* or *caustic soda.*

Other Properties. Reactions with hydrogen chloride and chlorine already given. Reduces copper oxide:—

$$3CuO + 2NH_3 = 3Cu + 3H_2O + N_2$$

Its solution in water contains ammonium hydroxide (NH_4OH), which precipitates various metals as hydroxides from solutions of their salts. E.g.

$$FeCl_3 + 3NH_4OH = Fe(OH)_3 + 3NH_4Cl$$

Nitrous oxide. Heat solid ammonium nitrate:—

$$NH_4NO_3 = 2H_2O + N_2O$$

Test. Re-ignites glowing splint.

Distinguished from oxygen by the fact that it does *not* form brown fumes with nitric oxide.

Nitric oxide. Add somewhat diluted nitric acid (1 : 1) to copper turnings:—

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$$

Test. Forms brown fumes on exposure to the air.

Other Properties. With ferrous sulphate forms a brown compound ($FeSO_4 \cdot NO$), which gives off nearly pure nitric oxide (99·8 per cent.) on heating.

Nitrogen dioxide. Add concentrated nitric acid to copper turnings:—

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2H_2O + 2NO_2$$

It is absorbed by concentrated sulphuric acid, but may be dried by passing it through calcium chloride.

Test. Reddish-brown colour and characteristic smell.

Other Properties. Easily liquefied (boiling-point 22° C.). It is a *mixed anhydride*, because with cold water it forms *two* acids

$$2NO_2 + H_2O = HNO_3 + HNO_2$$

(The nitrous acid readily breaks up:—

$$3HNO_2 = HNO_3 + H_2O + 2NO)$$

Dissociates when heated:—

$$N_2O_4 \rightleftarrows 2NO_2$$

(*b*) PREPARATION OF OXIDES—GENERAL METHODS

Oxides of Non-metals

Usually by heating the element in air or oxygen, e.g.

$$S + O_2 = SO_2$$
$$P_4 + 5O_2 = 2P_2O_5$$

Oxides of nitrogen are prepared by special methods (see above) which usually involve the reduction of nitric acid.

Oxides of Metals

(Especially calcium, magnesium, zinc, iron, lead, copper; this is the order in the electrochemical series, p. 391.)

(1) The metal may be heated in oxygen, e.g.

$$2Mg + O_2 = 2MgO$$

(2) The metal may be heated in a current of steam, e.g.

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$

(3) The metal may be dissolved in nitric acid, so forming the nitrate. This is then evaporated to dryness and decomposed by strong heating, e.g.

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2H_2O + 2NO_2$$
$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$$

(4) We may dissolve the metal in any suitable acid, and then add sodium carbonate solution to precipitate the carbonate. The latter is filtered, washed, dried and finally strongly heated. In most cases it decomposes, giving the oxide, e.g.

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$
$$ZnSO_4 + Na_2CO_3 = ZnCO_3 + Na_2SO_4$$
$$ZnCO_3 = ZnO + CO_2$$

(5) We may proceed exactly as in (4), but *via* the hydroxide instead of the carbonate (using sodium hydroxide solution instead of sodium carbonate), e.g.

$$ZnSO_4 + 2NaOH = Zn(OH)_2 + Na_2SO_4$$
$$Zn(OH)_2 = ZnO + H_2O$$

(6) The sulphate may be *strongly* heated, e.g.

$$ZnSO_4 = ZnO + SO_3$$

N.B. Method (1) works well with calcium and magnesium, and also with zinc and iron if the metals are in the form of shavings or thin wire. With lead and copper oxidation tends to be rather superficial. Method (2) applies to calcium, magnesium, zinc and iron. In the case of calcium, however, cold water acts quite freely (giving the hydroxide), so we should not use steam.

Methods (3), (4) and (5) apply to all the metals mentioned, and method (6) to all except the first two. This method is not very convenient, however, because such a high temperature is required.

(*c*) PREPARATION OF ACIDS—GENERAL METHODS

(i) Dissolve the corresponding anhydride in water, e.g.

CO_2	+	H_2O	=	H_2CO_3
Carbon dioxide or *Carbonic anhydride*				*Carbonic acid*
SO_3	+	H_2O	=	H_2SO_4
Sulphur trioxide or *Sulphuric anhydride*				*Sulphuric acid*

(ii) Heat a salt derived from the acid (e.g. a nitrate, if nitric acid is required) with sulphuric acid:—

$NaNO_3$	+	$H_2SO_4 = NaHSO_4$	+	HNO_3
Sodium nitrate				*Nitric acid*
$NaCl$	+	$H_2SO_4 = NaHSO_4$	+	HCl
Sodium chloride				*Hydrochloric acid*

(iii) Take the copper or lead salt of the required acid, dissolve in water and pass hydrogen sulphide through the solution, e.g.

$$CuSO_4 + H_2S = CuS + H_2SO_4$$

On filtering we get rid of the copper or lead, because these metals form insoluble sulphides. The filtrate is then boiled to expel excess of hydrogen sulphide and afterwards concentrated by evaporation.

(*d*) PREPARATION OF SALTS—GENERAL METHODS

See pp. 153–4.

(*e*) OXIDATION AND OXIDISING AGENTS

The term 'Oxidation' is discussed on p. 279. It will be convenient here to recall the definition at which we arrived.

Oxidation is *a chemical change involving either* (i) *gain of oxygen or other electro-negative element* (*or group*), *or* (ii) *loss of hydrogen or other electro-positive element.*

Some typical cases of oxidation are summarised below. In the cases marked α we have gain of oxygen; β=gain of some other electro-negative element (or group); γ=loss of hydrogen; δ=loss of some other electro-positive element.[1]

Oxygen. Combines directly with many elements, especially on heating, e.g.

$$C + O_2 = CO_2 \qquad (\alpha)$$

Steam is often used to oxidise carbon, iron, etc.

$$C + H_2O = CO + H_2 \qquad (\alpha)$$
$$3Fe + 4H_2O = Fe_3O_4 + 4H_2 \qquad (\alpha)$$

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[1] Of course the letters are not meant to be 'learnt.' In some cases, however, it is not quite easy to see *why* a given example is one of oxidation, and the letter will help to make the point clear.

Sulphuric acid (hot concentrated) oxidises certain non-metals, e.g. carbon and sulphur (p. 297)

$$C + 2H_2SO_4 = 2H_2O + 2SO_2 + CO_2 \qquad (\alpha)$$
$$S + 2H_2SO_4 = 2H_2O + 3SO_2 \qquad (\alpha)$$

It also oxidises metals, the oxide first formed being turned into sulphate by the excess of acid, e.g.

$$Cu + H_2SO_4 = CuO + H_2O + SO_2$$
$$CuO + H_2SO_4 = CuSO_4 + H_2O$$

i.e. (adding)

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2 \qquad (\beta)$$

Nitric acid acts similarly on the whole, but is much more powerful. In many cases it need not be hot, nor very concentrated.

Examples. (i) Rapid oxidation of carbon in sawdust, causing the substance to take fire. (α)

(ii)

$$Cu + 2HNO_3 = CuO + H_2O + 2NO_2$$
$$CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O$$

i.e. (adding)

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2H_2O + 2NO_2 \qquad (\beta)$$

(iii) In the presence of sulphuric acid it oxidises ferrous sulphate to ferric sulphate:—

$$2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O \qquad (\beta)$$

Chlorine oxidises elements by direct combination, e.g.

$$2P + 3Cl_2 = 2PCl_3 \qquad (\beta)$$

It oxidises hydrogen sulphide to sulphur:—

$$H_2S + Cl_2 = 2HCl + S \qquad (\gamma)$$

sulphurous acid to sulphuric:—

$$H_2SO_3 + H_2O + Cl_2 = 2HCl + H_2SO_4 \qquad (\gamma + \alpha)$$

and ferrous chloride to ferric:—

$$2FeCl_2 + Cl_2 = 2FeCl_3 \qquad (\beta)$$

Its bleaching action is also due to oxidation (p. 254). ($\gamma + \alpha$)

Manganese dioxide oxidises hydrochloric acid to chlorine

$$MnO_2 + 4HCl = 2H_2O + MnCl_2 + Cl_2 \qquad (\gamma)$$

Hydrogen peroxide oxidises lead sulphide to lead sulphate

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O \qquad (\alpha)$$

and potassium iodide to iodine:—

$$2KI + H_2O_2 = 2KOH + I_2 \qquad (\delta)$$

(*f*) REDUCTION AND REDUCING AGENTS

The term 'Reduction' is discussed on p. 279, where we arrived at the following definition. ***Reduction*** is *a chemical change involving either* (i) *loss of oxygen or other electro-negative element* (*or group*), or (ii) *gain of hydrogen or other electro-positive element.*

Oxidation is always accompanied by reduction, so examples of reduction can be found by going over the cases just given. Thus when steam oxidises carbon to carbon monoxide, it is evident that carbon *reduces* steam to hydrogen; when hydrogen peroxide oxidises lead sulphide to lead sulphate, the lead sulphide *reduces* hydrogen peroxide to water, and so on.

A few other typical examples of reduction are given below:

α=loss of oxygen.
β=loss of some other electro-negative element (or group).
γ=gain of hydrogen.
δ=gain of some other electro-positive element.[1]

Hydrogen is often used in the laboratory to reduce the oxide of a metal, e.g.

$$CuO + H_2 = H_2O + Cu \qquad (\alpha)$$

'Nascent' hydrogen will reduce a ferric salt (p. 115)

$$FeCl_3 + H = HCl + FeCl_2 \qquad (\beta)$$

Carbon is often used for the reduction of metallic oxides (on the large scale we have smelting; in the laboratory we heat on a charcoal block). E.g.

$$Pb_3O_4 + 2C = 2CO_2 + 3Pb \qquad (\alpha)$$

Carbon monoxide, formed in the blast furnace, is the reducing agent which acts upon the ferric oxide (p. 442):—

$$Fe_2O_3 + 3CO = 3CO_2 + 2Fe \qquad (\alpha)$$

Sulphur dioxide, in the lead chamber process, reduces nitrogen dioxide to nitric oxide (p. 293), sulphurous acid being first formed:—

$$SO_2 + H_2O = H_2SO_3 \qquad H_2SO_3 + NO_2 = H_2SO_4 + NO \qquad (\alpha)$$

It reduces chlorine to hydrogen chloride:—

$$H_2SO_3 + H_2O + Cl_2 = 2HCl + H_2SO_4 \qquad (\alpha + \gamma)$$

It reduces potassium permanganate to manganous sulphate. and potassium dichromate to chromium sulphate (p. 283). (α)

Its bleaching action is also due to reduction (p. 284) (α)

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[1] Cf. footnote on p. 520.

Hydrogen sulphide reduces ferric salts to ferrous salts, e.g.

$$2FeCl_3 + H_2S = 2HCl + 2FeCl_2 + S \qquad (\beta)$$

It reduces chlorine to hydrogen chloride:—

$$H_2S + Cl_2 = 2HCl + S \qquad (\gamma)$$

(*g*) TESTS FOR CARBONATES, SULPHATES, ETC.

A ***carbonate*** effervesces violently with cold dilute hydrochloric acid, carbon dioxide being evolved, e.g.

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

A ***sulphate*** gives a white precipitate with barium chloride, e.g.

$$Na_2SO_4 + BaCl_2 = BaSO_4 + 2NaCl$$

This precipitate is insoluble in hydrochloric acid. (*N.B.* Barium chloride gives a white precipitate with phosphates, sulphites, carbonates, etc., but it is only in the case of the sulphate that the precipitate is insoluble in hydrochloric acid.)

A ***sulphite*** gives off sulphur dioxide when warmed with hydrochloric acid (p. 281):—

$$Na_2SO_3 + 2HCl = 2NaCl + H_2O + SO_2$$

(For the white precipitate with barium chloride, see above.)

A ***nitrate*** gives brown fumes of nitrogen dioxide when mixed with copper and warmed with concentrated sulphuric acid. It also gives the 'brown ring' test. The explanation of these tests is given on pp. 340, 347.

A ***chloride*** (i) gives off hydrogen chloride when warmed with concentrated sulphuric acid (p. 245);

(ii) gives off chlorine when it is mixed with manganese dioxide and the mixture is then warmed with concentrated sulphuric acid (p. 246);

(iii) gives with silver nitrate a white precipitate of silver chloride, insoluble in nitric acid, but soluble in ammonia (p. 246), e.g.

$$NaCl + AgNO_3 = NaNO_3 + AgCl$$

A ***sulphide*** when warmed with hydrochloric acid will usually cause hydrogen sulphide to be evolved (smell of bad eggs; lead acetate paper blackened), e.g.

$$FeS + 2HCl = FeCl_2 + H_2S$$

(*h*) ACTION OF HEAT ON VARIOUS SUBSTANCES

Iodine. Physical change only (sublimes).

Carbon. When heated in air forms the dioxide:—

$$C + O_2 = CO_2$$

Phosphorus. When heated in air forms the pentoxide:—

$$P_4 + 5O_2 = 2P_2O_5$$

Magnesium. When heated in air forms the oxide:—

$$2Mg + O_2 = 2MgO$$

Magnesium oxide and ***zinc oxide.*** No chemical change in either case, but zinc oxide is yellow *while hot*; magnesium oxide remains white throughout.

Mercuric oxide is decomposed:—

$$2HgO = 2Hg + O_2$$

Barium peroxide gives off oxygen, leaving the monoxide:—

$$2BaO_2 = 2BaO + O_2$$

Manganese dioxide gives off oxygen when *strongly* heated, leaving trimanganic tetroxide:—

$$3MnO_2 = Mn_3O_4 + O_2$$

Lead monoxide melts but is not chemically changed. ***Lead dioxide*** (PbO_2) and ***red lead*** (Pb_3O_4) both give off oxygen, leaving the monoxide:—

$$2PbO_2 = 2PbO + O_2$$
$$2Pb_3O_4 = 6PbO + O_2$$

Lead nitrate decomposes, leaving the oxide (p. 349):—

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$

Copper nitrate decomposes in a similar way:—

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$$

Sodium nitrate decomposes, leaving the nitrite (p. 340):—

$$2NaNO_3 = 2NaNO_2 + O_2$$

Potassium nitrate behaves similarly.

Ammonium nitrate decomposes, giving nitrous oxide (p. 340)

$$NH_4NO_3 = 2H_2O + N_2O$$

Ammonium chloride sublimes, *apparently* without chemical change, but see p. 327.

Copper sulphate (hydrated) gives off water of crystallisation

$$CuSO_4 \cdot 5H_2O = CuSO_4 + 5H_2O$$

Many other hydrates behave in a similar way, e.g.

$$MgSO_4 \cdot 7H_2O = MgSO_4 + 7H_2O$$
$$Na_2CO_3 \cdot 10H_2O = Na_2CO_3 + 10H_2O$$

Calcium carbonate gives off carbon dioxide, and the oxide of the metal remains behind:—

$$CaCO_3 = CaO + CO_2$$

Most carbonates behave in a similar way, but sodium carbonate (Na_2CO_3) and potassium carbonate (K_2CO_3) are not changed at all. (Compare the action of heat on carbonates with its action on nitrates. In both cases, as a rule, the oxide remains behind, and in both cases the compounds of sodium and potassium behave exceptionally.)

Sodium bicarbonate decomposes below 100° C. (and therefore if boiled with water):—

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

Calcium bicarbonate (which exists only in solution) is easily decomposed:—

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2$$

Calcium hydroxide decomposes, leaving quicklime:—

$$Ca(OH)_2 = CaO + H_2O$$

Ferrous sulphate (hydrated). See p. 452.

Potassium chlorate gives off oxygen, and potassium chloride remains behind (p. 144):—

$$2KClO_3 = 2KCl + 3O_2$$

(*i*) ACTION OF WATER ON VARIOUS SUBSTANCES

Carbon dioxide. Some carbonic acid is formed:—

$$H_2O + CO_2 = H_2CO_3$$

Sulphur dioxide. Some sulphurous acid formed:—

$$H_2O + SO_2 = H_2SO_3$$

Sulphur trioxide. Sulphuric acid formed:—

$$H_2O + SO_3 = H_2SO_4$$

Phosphorus pentoxide. Metaphosphoric acid formed:—

$$H_2O + P_2O_5 = 2HPO_3$$

All the above four cases are examples of the formation of an acid by the action of water on an anhydride (p. 150).

(*N.B.* On boiling a solution of metaphosphoric acid it takes up another molecule of water, and *ortho*phosphoric acid is produced:—

$$HPO_3 + H_2O = H_3PO_4$$

Phosphorus trichloride. Phosphor*ous* acid formed, H_3PO_3 (phosphor*ic* acid being H_3PO_4):—

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$

Sodium (cold water).—Hydrogen is produced:—

$$2Na + 2H_2O = 2NaOH + H_2$$

Potassium. Similar to sodium:—

$$2K + 2H_2O = 2KOH + H_2$$

Calcium. Similar to sodium:—

$$Ca + 2H_2O = Ca(OH)_2 + H_2$$

Magnesium. Action with cold water is very slow. When the metal is heated in steam, hydrogen is produced freely:—

$$Mg + H_2O = MgO + H_2$$

Iron. The metal has to be heated in steam:—

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$

Note the general similarity in the last five reactions. Hydrogen is produced in every case, but the temperatures required vary a great deal. Sometimes the oxide of the metal is produced, sometimes the hydroxide.

Copper. This metal has no action on water or steam, no matter what the temperature may be.

Carbon. The mixture known as 'water-gas' is produced (p. 186):—

$$C + H_2O = CO + H_2$$

Copper sulphate (anhydrous) is hydrated:—

$$CuSO_4 + 5H_2O = CuSO_4 \cdot 5H_2O$$

Calcium oxide. The hydroxide is produced:—

$$CaO + H_2O = Ca(OH)_2$$

Ammonia. Some hydroxide is produced (p. 316):—

$$NH_3 + H_2O = NH_4OH$$

Calcium carbide. Acetylene is produced:—

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

(*j*) ACTION OF HYDROCHLORIC ACID ON VARIOUS SUBSTANCES

Zinc. Hydrogen is evolved:—

$$Zn + 2HCl = ZnCl_2 + H_2$$

Zinc oxide. The hydrogen that would otherwise be evolved is converted into water:—

$$ZnO + 2HCl = ZnCl_2 + H_2O$$

Calcium hydroxide. A salt and water formed:—

$$Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O$$

Calcium carbonate. A salt, water and carbon dioxide formed

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

N.B. The above four cases are examples of the general rule that a salt may be formed by the action of an acid on a metal, or on its oxide, hydroxide or carbonate (p. 153).

Sodium sulphite (warm dilute acid). Sulphur dioxide evolved (p. 278):—

$$Na_2SO_3 + 2HCl = 2NaCl + H_2O + SO_2$$

Other sulphites behave in the same way.

Potassium (or ***Sodium***) ***nitrite.*** Nitrous acid (HNO_2) is first formed

$$KNO_2 + HCl = KCl + HNO_2$$

(Some of the *anhydride* of this acid—nitrous anhydride, N_2O_3—is also formed, giving the solution a blue colour.)

The nitrous acid quickly decomposes, and the nitric oxide produced ($3HNO_2 = HNO_3 + H_2O + 2NO$) forms brown fumes with the oxygen of the air.

Ferrous sulphide. Hydrogen sulphide evolved:—

$$FeS + 2HCl = FeCl_2 + H_2S$$

Ammonia (i) (in solution) forms ammonium chloride:—

$$NH_4OH + HCl = NH_4Cl + H_2O$$

(ii) (gas, with gaseous hydrogen chloride) forms ammonium chloride (p. 318):—

$$NH_3 + HCl = NH_4Cl$$

Manganese dioxide (hot concentrated acid). Chlorine evolved

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$$

Lead dioxide (PbO_2) and ***red lead*** (Pb_3O_4) act in a similar way, and so do many other oxidising agents.

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Lead monoxide (PbO). Similar to the case of zinc oxide (see p. 527), but the lead chloride formed is only very slightly soluble.

Bleaching powder. Chlorine evolved (p. 255)

$$CaOCl_2 + 2HCl = CaCl_2 + H_2O + Cl_2$$

Notes. (i) In all the above cases the cold dilute acid could be used unless the contrary is mentioned.

(ii) Except in the case of manganese dioxide, lead dioxide and red lead, dilute sulphuric acid would give results very similar to the preceding, but of course sulphates would be formed in every case instead of chlorides. It would be a very good exercise for the student to rewrite the above equations, using sulphuric acid.

(*k*) ACTION OF SULPHURIC ACID ON VARIOUS SUBSTANCES

For the action of the cold dilute acid on a number of substances, see the note just given. In the following cases, the hot concentrated acid is supposed to be used:

Copper. ***Carbon.*** ***Sulphur.*** In all these cases the acid is reduced to sulphur dioxide (p. 297). Many other metals would behave similarly to copper:—

$$\begin{aligned} Cu + 2H_2SO_4 &= CuSO_4 + 2H_2O + SO_2 \\ C + 2H_2SO_4 &= CO_2 \quad + 2H_2O + 2SO_2 \\ S + 2H_2SO_4 &= \qquad\quad 2H_2O + 3SO_2 \end{aligned}$$

Sodium chloride. Hydrogen chloride evolved:—

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$

Potassium bromide. The action is similar *in the first instance*, hydrogen bromide (HBr) being produced. *Part* of this, however, is then oxidised (by the sulphuric acid) to bromine:—

$$H_2SO_4 + 2HBr = 2H_2O + SO_2 + Br_2$$

Potassium iodide. In this case the hydrogen iodide first produced is *nearly all oxidised*:—

$$H_2SO_4 + 8HI = 4H_2O + H_2S + 4I_2$$

Sodium nitrate. Nitric acid produced:—

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$

N.B. This is a good example of the general rule (p. 520) that to prepare an acid we heat the corresponding salt with sulphuric acid.

Oxalic acid. Carbon monoxide and dioxide evolved (p. 187)

$$H_2C_2O_4 = H_2O + CO + CO_2$$

Copper sulphate (hydrated) goes white, losing its water of crystallisation:—

$$CuSO_4 \cdot 5H_2O = CuSO_4 + 5H_2O$$

In the last two cases the sulphuric acid acts by removing the elements of water.

Alcohol. The final result (there is an intermediate stage) is loss of the elements of water, *ethylene* being evolved:—

$$C_2H_5 \cdot OH = H_2O + C_2H_4$$

Ethylene. This is an unsaturated compound (p. 198), and with sulphuric acid forms an 'addition product' called ethyl hydrogen sulphate:—

$$C_2H_4 + H_2SO_4 = C_2H_5 \cdot HSO_4$$

Hence sulphuric acid cannot be used to dry ethylene.

APPENDIX 2

NOTES ON FAMOUS CHEMISTS[1]

Aston, F. W. (1877–1945), Fellow of Trinity College, Cambridge. Received Nobel Prize (1922) for work on Isotopes (p. 506).

Avogadro, Amadeo (1776–1856). See p. 123.

Becher, John Joachim (1635–82). See p. 74.

Berzelius, J. J. (1779–1848), Swedish doctor and chemist. Firmly established the law of Multiple Proportions (1810). Spent ten years in determining the atomic and molecular weights of some 2000 elements and compounds, his work being a marvel of exactness. Proposed the simple system of representing atoms by their initial letters, etc. (p. 40). Was made a baron by the king of Sweden.

Black, Joseph (1728–99), Professor of Chemistry at Glasgow (later at Edinburgh). Carried out a famous research on chalk and related substances (quicklime, carbon dioxide, etc.), and on magnesia and related substances. Made great use of the balance, and was the first to emphasise the importance of quantitative measurement in chemistry.

Boyle, The Hon. Robert (1627–91), son of the Earl of Cork. Established the famous Law connecting the volume of a gas with its pressure (1660). Carried out many experiments to show that metals gain in weight on heating, but thought the gain was due to combination with particles of *fire* ('igneous corpuscles'). Was the first to give a clear definition of an element. Is regarded as the founder of modern chemistry.

Bunsen, Robert (1811–99), Professor of Chemistry at Heidelberg. Invented a number of well-known appliances—an electric cell, the 'grease-spot' photometer, bunsen burner ice-calorimeter, filter-pump, etc. Was one of the first workers in spectrum analysis, this being his chief contribution to the science of chemistry.

Cavendish, The Hon. Henry (1731–1810), first to recognise that hydrogen was a distinct substance. Showed that water is formed by the combination of two volumes of hydrogen with one of oxygen. Also showed how to identify gases by their physical properties, such as density and solubility in water. Seems to have isolated argon (pp. 88–9). Like Black, attached great importance to exact measurement.

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[1] In a few cases (e.g. Avogadro, Mme. Curie), the persons mentioned below have been famous as physicists rather than as chemists, but are included because they have made some important contribution to the science of chemistry.

Also made many researches in Physics, e.g. determined mean density of the earth.

Curie, Marie (1867–1935). Daughter of a Polish professor. See p. 502, and footnote, p. 530.

Dalton, John (1766–1844). See p. 37.

Davy, Sir Humphry (1778–1829), Professor of Chemistry at the Royal Institution (London). Discovered the anæsthetic properties of nitrous oxide (p. 346). Carried out much early work on electrolysis, and in the course of it isolated sodium and potassium (p. 424). Showed that chlorine is an element, and hence that its compound with hydrogen (hydrochloric acid) contains no oxygen—thus disproving the old idea, first entertained by Lavoisier, that oxygen is present in all acids.

Also made some researches on flame, which resulted in the invention of the Davy safety-lamp.

Faraday, Michael (1791–1867). Was attracted to the pursuit of science by hearing some lectures by Davy at the Royal Institution, where he himself later became Professor of Chemistry. He made valuable researches in chemistry, but actually his greatest discoveries were in the realm of physics (e.g. the principle of the dynamo). Discovered the laws of electrolysis, a subject which belongs both to chemistry and physics.

Gay-Lussac, Louis Joseph (1778–1850), Professor of Chemistry at the École Polytechnique (Paris).

Hooke, Robert (1635–1703). See pp. 73–4.

Lavoisier, Antoine Laurent (1743–94). Carried out many experiments showing that sulphur, phosphorus, tin and other elements gain in weight when heated in air, and in certain cases (e.g. tin) was able to prove that this gain is at the expense of the air. Hence became an opponent of the phlogistic theory (according to which elements *lose* something when heated in air). Priestley's experiment (mercury 'calx' decomposed on heating into mercury and 'dephlogisticated air') gave him the hint on which he based his famous experiment on the oxidation of mercury (pp. 75–6). He showed that mercury, when heated, absorbed something from the air, and that this 'something' could be completely recovered from the mercury 'calx.' This and other experiments dealt the phlogistic theory its death-blow, and cleared the way for modern chemistry.

Mayow, John (1645–79). See p. 74. He was a doctor of medicine and a friend of Robert Boyle.

Mendeléeff, Dmitri Ivanovitch (1839–1907). See p. 502.

Moseley, H. G. J. (1887–1915). Carried out a brilliant series of researches in which he showed that there was a close connection between the atomic number of an element (p. 505) and its X-ray spectrum. Killed in the trenches of Gallipoli, 10th August 1915.

Priestley, Joseph (1733–1804). Nonconformist minister, born near Leeds. Wrote many theological works, now almost forgotten. For some years (1772–79) was librarian to Lord Shelburne, and his best chemical work was done during this comparatively leisured period.

Prepared and examined a number of gases previously unknown, e.g. ammonia, nitrous oxide, hydrogen chloride and (most important of all) oxygen. His discovery of the very soluble gases hydrogen chloride and ammonia was due to the fact that he arranged for the preparation of gases over *mercury*. He thought that if he brought 'acid air' (hydrogen chloride) into contact with 'alkaline air' (ammonia), he would obtain a 'neutral air'—'perhaps the very same thing with common air.' To his great surprise he obtained ammonium chloride.

Exploded a mixture of hydrogen and air in a closed glass vessel, and noticed the deposit of dew. Cavendish followed up this observation and discovered the composition of water (p. 108). Similarly Priestley's discovery of oxygen, in the hands of Lavoisier, led to the overthrow of the phlogistic theory (pp. 75–7)—though Priestley himself remained a convinced phlogistonist until his death.

Made many enemies owing to his supposed sympathy with revolutionary doctrines, and emigrated to America, where he spent the last ten years of his life.

Ramsay, Sir William (1852–1916). Discovered argon in the atmosphere (1895), and, later, the rare gases krypton, xenon and neon. See pp. 89, 91.

Rayleigh, Lord (1842–1919). Collaborated with Ramsay in the discovery of argon.

Rey, Jean (?–1645). See p. 73.

Scheele, Karl Wilhelm (1742–86). Swedish apothecary. Best known as the discoverer of chlorine (1774), but actually he prepared and investigated a very large number of substances. Discovered oxygen at least a year before Priestley, though neither man knew of the other's work. Among his discoveries were many organic compounds (e.g. tartaric acid from grapes, citric acid from lemons and malic acid from apples). See also pp. 258–9.

Stahl, George Ernst (1660–1734). German chemist and physician. See pp. 74–77.

APPENDIX 3

GENERAL QUESTIONS

N.B. *The scope of the following questions is such that it is hardly possible to answer them by the study of any one particular chapter. They are, however, very suitable as exercises when the work as a whole is being reviewed.*

1. In *four* of the following pairs of terms, distinguish carefully between the terms in each pair and explain the meaning of each term: (a) *atom* and *ion*; (b) *evaporation* and *distillation* of a solution; (c) *hydrocarbon* and *carbohydrate*; (d) *hydrate* and *hydroxide*; (e) *acid salt* and *normal salt*. *Lond.*

2. Explain the meaning of the following terms: (*a*) a filtrate; (*b*) an indicator; (*c*) an exothermic reaction; (*d*) vapour density; (*e*) molecular weight.

The atomic weight of phosphorus is 31. When vaporised its vapour density is 62. How many atoms of phosphorus are there in one molecule of the vapour? Give reasons for your answer. *J.M.B.*

3. Define or explain the following terms: (*a*) a deliquescent substance; (*b*) a dibasic acid; (*c*) a solubility curve; (*d*) an alloy; (*e*) a dehydrating agent. Give *one* example of each. *Camb.*

4. What do you understand by the following terms? Illustrate your answer by giving *one* example of each: (*a*) an electrolyte; (*b*) a hydrocarbon; (*c*) an oxidising agent; (*d*) a base; (*e*) an efflorescent salt. *Camb.*

5. Explain what is meant by the following terms, and give *one* example of each: (*a*) double decomposition; (*b*) catalytic decomposition; (*c*) thermal dissociation; (*d*) incandescence; (*e*) exothermic reaction; (*f*) a hydrocarbon. *Lond.*

6. Define *five* of the following terms and describe briefly an actual example to illustrate each definition: catalyst, deliquescence, synthesis, sublimation, electrolysis, allotropy, acid anhydride. *Brist.*

7. Name *one* example of each of the following: (*a*) a gas which is denser than air; (*b*) a gas which is less dense than air; (*c*) a deliquescent solid; (*d*) a liquid which is very volatile; (*e*) a dibasic acid; (*f*) an acidic anhydride. *J.M.B.*

8. Give the *name* (not the symbol) of: (*a*) a metal which readily burns in air; (*b*) a metal which displaces hydrogen from cold water; (*c*) a metal which displaces copper from a solution of copper sulphate; (*d*) a metal which burns spontaneously in chlorine; (*e*) a non-metal which burns readily in air; (*f*) a non-metal which displaces iodine from a solution of potassium iodide. *J.M.B.*

9. Name one example in each case of a *salt* which on heating: (*a*) loses water of crystallisation; (*b*) gives nitrogen; (*c*) gives a brown gas; (*d*) gives carbon dioxide and water vapour. *J.M.B.*

10. Give the names and formulæ of: an alkali, a salt, a nitrogenous fertilizer, a substance which sublimes. *O.C.* (*part*)

11. Name and give the formulæ of: (i) a gaseous compound which is very soluble in water; (ii) a black solid compound; (iii) four components of the air. *O.C.* (*part*)

12. Give the chemical name and formula of: (i) a red metallic oxide; (ii) a white insoluble metallic hydroxide; (iii) an insoluble metallic sulphate; (iv) a coloured metallic carbonate. *W.J.* (*part*)

13. Name: (i) *two* solid non-metals; (ii) *two* gases that cannot be collected over water; (iii) *two* hydrated salts, one colourless and one coloured; (iv) *two* gases which are lighter than air. *W.J.* (*part*)

14. What do you understand by the term *reduction*?

How would you proceed to reduce the following: (*a*) litharge; (*b*) a solution of potassium permanganate; (*c*) a solution of a ferric salt; (*d*) silica (sand)? *Lond.*

15. (i) Define oxidation.

(ii) $2FeCl_3 + SO_2 + 2H_2O = 2FeCl_2 + 2HCl + H_2SO_4$

State which of the reactants in the above equation is the oxidising agent. *O.C.* (*part*)

16. (*a*) Give different examples, *one* in each case of: (i) a reduction involving a loss of oxygen; (ii) an oxidation involving a loss of hydrogen; (iii) an oxidation involving a change of valency of an element; (iv) a reduction involving a loss of a non-metallic element other than oxygen.

(An equation is required for each reaction.)

(*b*) A white powder is known to be either an oxidising agent or a reducing agent. Describe *two* tests which would enable you to decide which it is. *Camb.*

17. Name the gas, or gases, given off when each of the following substances is strongly heated: lead carbonate; ammonium nitrate; anhydrous copper nitrate; potassium nitrate; sodium bicarbonate. *W.J.* (*part*)

18. Write an account of the effect of heat on: (*a*) potassium chlorate; (*b*) sodium bicarbonate; (*c*) sodium nitrate; (*d*) ammonium nitrate; (*e*) copper nitrate; (*f*) temporarily hard water.

What is the effect of passing pure dry hydrogen over a sample of the residue in (*e*) heated strongly? *Lond.*

19. Describe the action of heat on the following substances, mentioning any colour changes that occur and giving equations for any chemical decompositions that take place: (*a*) zinc carbonate; (*b*) lead dioxide; (*c*) washing soda; (*d*) potassium nitrate; (*e*) hydrated copper nitrate; (*f*) gelatinous silicic acid. *Lond.*

20. Write the equations for the reactions which take place, name the products formed, and state what you would observe when the following substances are heated: (*a*) potassium chlorate; (*b*) lead nitrate; (*c*) ferrous sulphate crystals; (*d*) mercuric oxide; (*e*) ammonium nitrate; (*f*) ammonium chloride. *Camb.*

21. State what you observe, name the products and explain the changes that take place, in each of the following reactions: (*a*) Hydrogen sulphide is bubbled into chlorine water. (*b*) A piece of marble is dropped into dilute sulphuric acid. (*c*) A stick of sodium hydroxide is left exposed to the air. (*d*) Ammonium hydroxide solution is added gradually, until it is in excess, to a solution of copper sulphate. (*e*) A piece of red-hot charcoal is dropped into a tube containing a little warm, fuming nitric acid. *W.J.*

22. State carefully what you would observe, and name the products, in each of the following experiments (equations must not be given): (*a*) A current of electricity is passed through a solution of copper sulphate, using platinum electrodes. (*b*) Ferrous sulphate crystals are heated in a test-tube. (*c*) Excess zinc is added to a solution of copper sulphate. (*d*) Copper is heated with concentrated sulphuric acid; the mixture is then cooled and finally poured into water. (*e*) A mixture of common salt and ammonium chloride is heated in a test-tube. *W.J.*

23. In any *four* of the following experiments describe the changes that take place, particularly noting any visible effects, name the products and give equations: (*a*) Carbon dioxide is continuously bubbled into lime-water. (*b*) Dilute nitric acid is allowed to react on copper. (*c*) A filter-paper, soaked in a solution of phosphorus in carbon disulphide, is exposed to the air. (*d*) A lighted taper is plunged into a gas-jar filled with carbon monoxide. (*e*) Solutions of silver nitrate and of sodium chloride are mixed and the product exposed to light. (*f*) A solution of sodium hydroxide is added slowly to a solution of aluminium sulphate, until the sodium hydroxide is in excess. *Brist.*

24. Describe what happens when the following operations are performed: (*a*) Chlorine water is exposed to sunlight. (*b*) Washing soda crystals are heated. (*c*) Concentrated nitric acid is added to copper. (*d*) A solution of lead nitrate is added to dilute hydrochloric acid. (*c*) Water is added to baking powder. *Camb.*

25. Describe and explain what happens when: (i) a candle burns in a jar of chlorine; (ii) water is added to quicklime (calcium oxide); (iii) concentrated sulphuric acid is mixed with potassium nitrate and heated. *Camb.*

26. Explain how by a chemical test you would distinguish between the two substances in each of the following pairs. (Remember: (i) that only one chemical test is required for each pair of substances, but you must state the results of that test on each substance of the pair; (ii) that the evolution of any invisible gas must be confirmed by some test.) (*a*) Ammonium sulphate and sodium carbonate; (*b*) potassium chloride and barium nitrate; (*c*) solid sodium peroxide and anhydrous copper sulphate; (*d*) solutions of ferrous chloride and ferric chloride. *J.M.B.*

27. Show by what laboratory tests you could distinguish between the following pairs of *solutions:* (*a*) sodium hydroxide and calcium hydroxide; (*b*) ammonium chloride and sodium chloride; (*c*) ferrous sulphate and calcium sulphate; (*d*) potassium nitrate and silver nitrate; (*e*) copper sulphate and copper nitrate. *Dur.*

28. For each of the pairs of substances (*a*) to (*e*) describe *one* chemical test which, when applied to each of the substances in the pair, will enable you to distinguish between them. In each case, state what is observed during the test and what has taken place. (*a*) Copper oxide and powdered charcoal; (*b*) sodium nitrate and sodium chloride; (*c*) red mercuric oxide and red lead; (*d*) magnesium and iron; (*e*) a solution of lead nitrate and a solution of potassium nitrate. *W.J.*

29. How would you distinguish between the following pairs of substances: (*a*) ammonium carbonate and ammonium chloride; (*b*) red lead oxide and red mercuric oxide; (*c*) black copper oxide and powdered carbon; (*d*) potassium chlorate and potassium chloride; (*e*) lead sulphate and lead chloride? *Dur.*

30. Give *two* chemical tests to distinguish each of the following pairs: (i) calcium carbonate and calcium hydroxide; (ii) cuprous oxide and mercuric oxide; (iii) ammonium sulphate and sodium sulphite; (iv) manganese dioxide and ferrous sulphide; (v) oxygen and ozonised oxygen. *Scot. L.C.*

31. State how you would prove the presence of the following impurities in the substances named below: (*a*) calcium carbonate in quicklime (calcium oxide); (*b*) sodium sulphate in caustic soda (sodium hydroxide); (*c*) hydrogen sulphide in hydrogen; (*d*) potassium chloride in saltpetre (potassium nitrate). Give *one* chemical test in each case. *Camb.*

32. From tests described below *name* each of the given substances:

Substance A. 1. On warming with sodium hydroxide solution gives a gas which turns moist red litmus paper blue.

2. When dissolved in water and mixed with dilute nitric acid and silver nitrate solution gives a white precipitate.

Substance B. 1. When dissolved in water and mixed with a solution of ammonia gives a deep blue solution.

2. When dissolved in water and mixed with hydrochloric acid and barium chloride solution gives a white precipitate.

Substance C. 1. When heated on a charcoal block gives a soft malleable bead which marks paper.

2. When dissolved with ferrous sulphate in water, the careful addition of concentrated sulphuric acid produces a brown layer at the junction of the two liquids.

Substance D. 1. When added to sodium carbonate produces a colourless gas which turns lime-water milky.

2. When added to copper turnings reacts vigorously to give acidic brown fumes and a blue solution. *J.M.B.*

33. Describe, giving essential experimental details, the procedure you would follow to obtain: (i) crystals of cupric chloride from copper sulphate; (ii) ammonium chloride from ammonium nitrate; (iii) sodium bisulphate from sodium hydroxide; (iv) barium sulphate from barium carbonate. (Equations should be given for each reaction.) *Scot. L.C.*

34. Give brief descriptions of how you would convert: (*a*) iron into ferric oxide; (*b*) copper into copper sulphate crystals; (*c*) zinc into zinc sulphide. *Camb.*

35. What reagents would you use to dry: (i) ammonia; (ii) sulphur dioxide; (iii) carbon dioxide; (iv) hydrogen sulphide; (v) hydrogen chloride? *O.C.* (*part*)

36. State briefly how you would separate from each of the following mixtures a specimen of the substance *first* named: (*a*) ammonium chloride and sodium chloride; (*b*) sulphur and iron filings; (*c*) nitrogen and carbon dioxide; (*d*) hydrogen and ammonia. *J.M.B.*

37. How would you obtain a pure sample of the first-named substance *only*, from each of the following mixtures: (*a*) ammonium chloride and sodium chloride; (*b*) potassium nitrate and powdered chalk; (*c*) powdered copper and copper oxide; (*d*) carbon dioxide and carbon monoxide; (*e*) potassium chlorate and sodium chloride? *W.J.*

38. Explain the following: (*a*) a white deposit, usually called 'fur,' is found inside kettles in some parts of the country; (*b*) a colourless gas is evolved when chlorine water is exposed to sunlight; (*c*) a pink rose petal loses its colour when placed in moist sulphur dioxide gas; (*d*) a brown colour develops in a jar of nitric oxide after it has been opened to the air; (*e*) a white smoke is produced when ammonia and chlorine are mixed. *Camb.*

39. Explain each of the following facts: (*a*) A lump of quicklime gets very hot and crumbles when a little water is added to it. (*b*) Grass stains on clothing can be removed with methylated spirit. (*c*) Baking powder makes a cake 'light.' (*d*) When the air inlet of a bunsen burner is opened and the gas supply is reduced, the flame 'strikes back.' *Camb.*

40. Explain the following facts: (*a*) When water is added to a mixture of sodium bicarbonate and sodium hydrogen sulphate there is a vigorous effervescence. (*b*) If a stream of ammonia is passed through a red hot tube, the gas can then be burnt in air. (*c*) When iron is smelted, limestone is added to blast furnace charges. (*d*) When a beaker of cold water is placed over a bunsen burner, drops of water are formed on the surface of the beaker. If the air-holes of the bunsen are closed, then soot is deposited. (*e*) Nitric oxide turns brown when exposed to air. *Camb.*

ANSWERS TO NUMERICAL EXAMPLES

Chapter 5, pp. 53–4

1. (i) 63·6; (ii) 86·6; (iii) 27·3; (iv) 52·9.

2. (i) Na, 27·1; N, 16·5; O, 56·5. (ii) Ca, 40; C, 12; O, 48. (iii) Ag, 63·5; N, 8·2; O, 28·2. (iv) Pb, 68·3; S, 10·6; O, 21·1. (v) Ca, 36·0; Cl, 64·0. (vi) Ca, 54·1; O, 43·2; H, 2·7.

3. (i) 51·2; (ii) 36·0; (iii) 49·3; (iv) 62·9; (v) 43·9; (vi) 20·9.

4. (i) CO_2; (ii) FeS; (iii) P_2O_5; (iv) $AgNO_3$; (v) KNO_3; (vi) $CuSO_4 \cdot 5H_2O$.

5. (i) CO; (ii) PbS; (iii) Al_2O_3; (iv) Na_2CO_3; (v) H_2SO_4; (vi) $ZnSO_4 \cdot 7H_2O$.

6. 108 gm. **7.** 4 gm. **8.** 49 gm. **9.** 18·5 gm.

10. (i) 0·88 gm.; (ii) 1·3 gm. **11.** 32·2 gm. **12.** 5·6 gm.

13. $M_2(SO_4)_3 \cdot 18H_2O$.

Chapter 6, pp. 68–72

1. (i) 266 c.c.; (ii) 364 c.c.; (iii) 517 c.c.

2. (i) 31·2 l.; 24·9 l.; 32·1 l. **3.** (*a*) 307° C.; (*b*) 1480 mm.

4. 144 cm. **5.** 117 cm. **8.** (i) 32·7; (ii) 9·0; (iii) 12·0.

9. 100. **10.** (i) 32; (ii) 103·4; (iii) 18·67.

11. 12·2; 31·6; 32·9.

12. 1*st boy*. (i) 519 c.c.; (ii) 0·0467 gm.; (iii) 32·1.
2*nd boy*. (i) 699 c.c.; (ii) 0·0629 gm.; (iii) 31·8.
3*rd boy*. (i) 845 c.c.; (ii) 0·0761 gm.; (iii) 32·9.

13. 1*st boy*. (i) 510 c.c.; (ii) 0·0459 gm.; (iii) 32·7.
2*nd boy*. (i) 686 c.c.; (ii) 0·0617 gm.; (iii) 32·4.
3*rd boy*. (i) 830 c.c.; (ii) 0·0747 gm.; (iii) 33·5.

14. 31·7. **15.** 107·8.

16. (*a*) Oxygen, 88·9%, hydrogen, 11·1%; (*b*) 31·75.

17. (i) MCl_3; (ii) $M_2(SO_4)_3$; (iii) 18·3. 36·6 gm. **19.** 3.

20. M_2O_3; $M_2(SO_4)_3$. **21.** (i) 29·67; (ii) 4; (iii) 118·7.

22. (*a*) (i) 18·67, (ii) 57, (iii) 56·0; (*b*) M_2O_3.

23. 65·0. **24.** 40·5; $M(OH)_2$; MCO_3.

25. (i) M_2O_3; (ii) $M(OH)_3$; (iii) $M_2(SO_4)_3$, 9. **26.** 12; 12.

27. 103·5; 51·7; 207·0; 2; 4; MO, MO_2.

28. (i) 29·76; (ii) 119·0. MCl_4. **29.** 18·67; 28·07.

Chapter 7, p. 77

1. 10·2 oz.

Chapter 8, pp. 91–2

1. O, 22·92; N, 77·08.

2. $N_{15}O_4$ (approx.); $N_{26}O_7$ is much closer. **3.** 35.

Chapter 9, pp. 109–110

1. Oxygen, 88·9; hydrogen, 11·1.

2. (i) Oxygen, 88·9%; hydrogen, 11·1%. (ii) The same. **7.** 5.

Chapter 10, p. 119

2. 43·9. **3.** $MgSO_4 \cdot 7H_2O$.

Chapter 11, pp. 132–5

A.

3. 4·48 *l*. **4.** 17. **5.** CH; C_6H_6. **6.** 16 gm.

8. 28. **10.** 28; 4. **11.** 12.

B.

1. 18·25, 35·5, 14, 9.

2. Acetylene, nitric oxide, hydrogen sulphide, argon, carbon dioxide, chlorine. **3.** 280 c.c.

4. Nitrogen v, oxygen $\frac{1}{2}v$; hydrogen $\frac{1}{2}v$, chlorine $\frac{1}{2}v$; hydrogen v, oxygen $\frac{1}{2}v$.

5. 250 c.c.; (*a*) 50 c.c. steam, 50 c.c. CO_2; 200 c.c. N_2 (*b*) 50 c.c. CO_2; 200 c.c. N_2.

6. (i) 1120 c.c.; (ii) 336 c.c.; (iii) 448 c.c. hydrogen.

7. 5 c.c., 10 c.c.; 15 c.c., 10 c.c. **8.** 1344 c.c.

9. (i) 0·088 gm.; (ii) 44·8 c.c.

10. (i) 400 ml. oxygen; (ii) 200 ml. ammonia.

11. 2. **12.** $C_4H_{10}O$. **13.** C_2H_4. **14.** 44.

Chapter 12, pp. 141–2

2. 125 sec. **5.** 72. **6.** (*a*) 25·2 (*b*) 50·4. **7.** 100·43.

Chapter 13, pp. 154–5

3. 3360 c.c. **7.** (*a*) 7; (*b*) 4; (*c*) 28.

Chapter 14, pp. 161–2

3. 20 c.c.; (*a*) 90 c.c.; (*b*) 0·227 gm. **5.** 329 c.c.

6. 6·30 gm.

Chapter 15, pp. 170–1

2. 3·00. **3.** 3·04.

Chapter 16, pp. 183–4

3. 9·12; 560 c.c. **6.** 834 c.c. **7.** 1·44 *l.*; 6·31 gm.

Chapter 17, pp. 193–4

3. 45 gm.; (i) 8 *l.*; (ii) 8·52 *l.*

4. 25 c.c. (15 c.c. oxygen, 10 c.c. CO_2).

7. 5 *l.*; 1 *l.* CO_2, 1 *l.* steam, 4 *l.* N_2. **8.** CO 50%, H_2 50%.

Chapter 18, pp. 205–6

1. Methane $33\frac{1}{3}$%, hydrogen $66\frac{2}{3}$%. **2.** Methane.

3. (*a*) 15; (*b*) 238 c.c.; (*c*) 1050 c.c. **4.** (i) 11·6 *l.*; (ii) 37 gm.

5. Methane 55·6%; ethylene 44·4%. **7.** 100 c.c., 200 c.c.

Chapter 20, pp. 235–6

1. 504 c.c.; 0·45 gm. **7.** 400 cu. ft.

Chapter 21, pp. 246–7

2. 7·3 gm.; 4·79 *l.* **6.** H, 2·7; Cl, 97·3.

7. 1·34 *l.*; 2·98 gm. **9.** 58·5.

Chapter 22, pp. 259–260

8. No; 55·9 per cent. **9.** $KMnO_4$.

10. 1·65 tons; 1·13 tons.

Chapter 23, p. 269

3. 157 c.c. **6.** 59·5. **7.** 1·79 *l.*

Chapter 24, p. 276

2. $CaSO_4$.

Chapter 25, pp. 285–6

10. 477 *l.* **11.** 32 gm.; (i) 11·2 *l.*; (ii) 12·47 *l.*

12. 284 c.c.

Chapter 26, pp. 301–2

6. 21·3 cwts. **12.** 2. **13.** $Na_2CO_3 \cdot 10H_2O$.

Chapter 27, pp. 311–12

1. 0·16 gm. **9.** 235 c.c. **10.** 169·2 c.c.

Chapter 28, pp. 330–1

3. 23·7 c.c. **4.** N, 82·3; H, 17·7; NH_3.

9. $N_2H_4O_3$ ($=NH_4NO_3$). **11.** 90 c.c.

Chapter 29, pp. 342–3

5. (*a*) 8·40 gm.; (*b*) 5·14 gm. **6.** KNO_3, 74·8; C, 13·3; S, 11·9.
8. (i) 72·8 *l.*; (ii) 24·3 *l.*; (iii) 24·3 *l.*

Chapter 30, pp. 355–6

2. 57·14 gm. **3.** $N_2H_4O_3$; ammon. nitrate. **5.** NO.
11. (i) 30·9; (ii) 5·65.

Chapter 31, p. 370

3. 5 tons. **4.** $NaH_2PO_2 \cdot H_2O$.

Chapter 34, pp. 407–9

4. 0·54 gm.
5. (*a*) 500 c.c. oxygen; (*b*) 2·88 gm. copper; (*c*) 1000 c.c. hydrogen, 500 c.c. oxygen; (*d*) 2·07 gm. sodium, 1000 c.c. chlorine.
8. 31·8. **9.** 10 amps. **10.** 753 c.c. **11.** 168 c.c.

Chapter 36, pp. 431–2

5. 23·01 gm. (*not* 22·70 gm.). **11.** 60·0.
12. (*a*) 1·12 *l.*; (*b*) 1·19 *l.*

Chapter 37, pp. 458–9

3. (*a*) Al_4C_3; (*b*) 5·04 *l.* **9.** 4·03 gm. **10.** $2Fe_2O_3 \cdot 3H_2O$.

Chapter 38, pp. 479–481

1. 34·6. **3.** 39 gm.; (*d*) 64; (*e*) 1. **8.** 102·9.

Chapter 39, pp. 493–7

1. 49; 53; 143; 36·5; 84; 56. **2.** 6·31 gm.; 1190 c.c.
3. 49 gm.; 9·12 gm.; 40 gm.; 1·32 gm.
4. (i) 0·1 N; (ii) 0·2 N; (iii) 0·164 N; (iv) 0·0322 N; (v) 0·2 N.
5. 84·7; 37. **6.** 120 c.c. **7.** 84 c.c. **8.** 61·25.
9. 4·54. **10.** 4·55N. **11.** N/5; 9·8 gm./*l.* **12.** 13·3 c.c.
13. 0·042 N; 1·55 gm./*l.* **14.** 0·8 N; 29·2, 39·2, 50·4 gm.
15. 400 c.c. **16.** 2. **17.** 50; 40.
18. (i) 1·26 gm.; (ii) 0·98 gm.; 16·9. **19.** 46·6.
20. (*a*) 2N; 1·6N; (*b*) 64 gm.; (*c*) 24 gm., 24·3 *l.*
21. 2; 41; 23. **22.** 28·0; 56·0. **23.** 12·0; 56·1. **24.** 20.
25. 418 c.c.; 2·05 gm. **26.** (*a*) 485 c.c.; (*b*) 400 c.c.
27. 1·36 gm. **28.** 18·2; 90·2. **29.** 0·142N; 4·48 gm./*l.*
30. 30·6 gm.

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N.B. (1) *The principal references are indicated by* **heavy type.**
(2) *Only the* first page *of a reference is given, unless otherwise stated.*

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	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170						4	9	13	17	21	26	30	34	38
						0212	0253	0294	0334	0374	4	8	12	16	20	24	28	32	36
11	0414	0453	0492	0531	0569						4	8	12	15	19	23	27	31	35
						0607	0645	0682	0719	0755	4	7	11	15	19	22	26	30	33
12	0792	0828	0864	0899	0934						3	7	11	14	18	21	25	28	32
						0969	1004	1038	1072	1106	3	7	10	14	17	20	24	27	31
13	1139	1173	1206	1239	1271						3	7	10	13	16	20	23	26	30
						1303	1335	1367	1399	1430	3	7	10	13	16	19	22	25	29
14	1461	1492	1523	1553	1584						3	6	9	12	15	19	22	25	28
						1614	1644	1673	1703	1732	3	6	9	12	15	17	20	23	26
15	1761	1790	1818	1847	1875						3	6	9	11	14	17	20	23	26
						1903	1931	1959	1987	2014	3	6	8	11	14	17	19	22	25
16	2041	2068	2095	2122	2148						3	5	8	11	14	16	19	22	24
						2175	2201	2227	2253	2279	3	5	8	10	13	16	18	21	23
17	2304	2330	2355	2380	2405						3	5	8	10	13	15	18	20	23
						2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648						2	5	7	9	12	14	16	19	21
						2672	2695	2718	2742	2765	2	5	7	9	11	14	16	18	21
19	2788	2810	2833	2856	2878						2	4	7	9	11	13	16	18	20
						2900	2923	2945	2967	2989	2	4	6	8	11	13	15	17	19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

LIST OF THE COMMONER ELEMENTS AND THEIR ATOMIC WEIGHTS

Element	Symbol	Atomic Weight (approximate)	Atomic Weight * (more exact)
Aluminium	Al	27	26·98
Antimony (stibium)	Sb	122	121·76
Argon	A	40	39·944
Arsenic	As	75	74·91
Barium	Ba	137	137·36
Bismuth	Bi	209	209·00
Boron	B	11	10·82
Bromine	Br	80	79·916
Cadmium	Cd	112	112·41
Calcium	Ca	40	40·08
Carbon	C	12	12·011
Chlorine	Cl	35·5	35·457
Chromium	Cr	52	52·01
Cobalt	Co	59	58·94
Copper (cuprum)	Cu	64	63·54
Fluorine	F	19	19·00
Gold (aurum)	Au	197	197·0
Helium	He	4	4·003
Hydrogen	H	1	1·0080
Iodine	I	127	126·91
Iridium	Ir	192	192·2
Iron (ferrum)	Fe	56	55·85
Lead (plumbum)	Pb	207	207·21
Lithium	Li	7	6·94
Magnesium	Mg	24	24·32
Manganese	Mn	55	54·93
Mercury (hydrargyrum)	Hg	201	200·61
Neon	Ne	20	20·183
Nickel	Ni	59	58·69
Nitrogen	N	14	14·008
Oxygen	O	16	**16**
Phosphorus	P	31	30·975
Platinum	Pt	195	195·23
Potassium (kalium)	K	39	39·100
Radium	Ra	226	226·05
Selenium	Se	79	78·96
Silicon	Si	28	28·09
Silver (argentum)	Ag	108	107·880
Sodium (natrium)	Na	23	22·991
Strontium	Sr	88	87·63
Sulphur	S	32	32·066
Tellurium	Te	128	127·61
Thorium	Th	232	232·05
Tin (stannum)	Sn	119	118·70
Tungsten (wolframium)	W	184	183·92
Uranium	U	238	238·07
Zinc	Zn	65	65·38

* Extracted from the table of *International Atomic Weights,* 1953

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